The Use of Isothermal Membrane Distillation in Tomato Processing

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Declaration

The study presented in this thesis is original and was completed while I was enrolled as a research student at the School of Life Sciences, Victoria University of Technology. The work presented in this thesis is entirely my own and to the best of my knowledge has not been submitted in whole or as a part of any other degree or diploma at any other University. The assistance received in this thesis by previously published material, has been acknowledged and properly referenced.

Amita Bernardi

2002

This thesis is dedicated to my husband Allan and two children, André and Alanah who are my constant companions. I am eternally grateful for their support and understanding during the period of this research.

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Presentation and Publications

Bernardi A, Hogan P and Kyle W S A (1996). Thermal inactivation of enzymes in Australian Varieties of Roma Tomatoes. Paper presented at the 29th AIFST conference 5-8th May 1996, Gold Coast.

Bernardi A, Hogan P and Kyle W S A (1997). Membrane processes for the production of high quality tomato concentrates. Abstract accepted for a paper at the 30th AIFST conference 4-9th of May 1997, Perth.

Bernardi A and Kyle W S A (1998). The production of improved quality tomato concentrates by the use of linked membrane processes. Paper presented at the 31st AIFST conference 26-29th April 1998, Melbourne.

Bernardi A and Kyle W S A (2002). The effect of blanching and freezing on pH, titratable acidity and enzymes in tomatoes at different break temperatures. International Journal of Food Science and Technology (in preparation).

Abstract

This thesis is an investigation of tomato paste preparation by the use of isothermal membrane distillation (IMD). Traditional vacuum evaporation processes used for tomato paste production operate at high temperatures for long periods and can cause thermal damage to heat sensitive components and loss of volatile flavour and aroma compounds. In addition to these changes, other undesirable browning reactions such as the formation of hydroxymethylfurfural (HMF) can occur. IMD is a low temperature membrane process used for the concentration of heat sensitive pharmaceutical products. Its use in the food commenced with the concentration of grape juice for winemaking. Although IMD can concentrate grape juice up to 70% total solids level, its use is limited to clarified juices due to membrane materials currently available. Tomato juice contains a considerable amount of suspended solids hence clarification of the juice is necessary for subsequent concentration processes. Primary clarification involved the use of centrifugation to fractionate the tomato juice into solids and serum components. The tomato serum was unsuitable for concentration by IMD since it still contained low levels of suspended solids hence required secondary clarification. Ultrafiltration (UF) or microfiltration (MF) were two membrane processes used for secondary clarification of tomato serum. The resultant UF or MF permeates were subsequently processed by IMD or by linked reverse osmosis (RO)-IMD processes. The linked processes were chosen because RO had the capability of preconcentrating the IMD feed which reduced the duration of the IMD process. The IMD concentrate was then recombined with the tomato solids obtained from centrifugation to produce two different tomato pastes of 25% and 30% total solids levels. The recombined pastes were then compared with commercial concentrates by the use of taste panels. Since tomato pastes are often used on pizza bases, the pastes were also assessed on pizza bases. Physiochemical properties of colour, consistency, ascorbic acid and hydroxymethylfurfural of the recombined and commercial pastes were also examined and compared. The microbiological status of these pastes was also assessed to confirm that they were safe for consumption.

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List of Abbreviations

a* (+)	redness
a*(-)	greeness
∝	alpha
β	beta
b* (+)	yellowness
b*(-)	blueness
CA	cellulose acetate
cfu	colony forming units
cm	centimetre
FC	forced circulation evaporator type
FF	falling film evaporator type
FSANZ	Food Standards Australia New Zealand
g	gram
g	acceleration due to gravity
γ	gamma
h	hectare
HPLC	high-performance liquid chromatography
hr	hour
IMD	isothermal membrane distillation
kg	kilogram
kg/h	kilogram per hour
kha	kilohectare
kJ	kilojoule
kPa	kilopascal
kt	kilotonne
kW	kilowatt
L*	luminescence during colour measurement
L	litre
LSD	Least significant difference
M	molarity

$m	million dollars
m^2	square metre
m^3	cubic metre
MC	mixed circulation evaporator
MF	microfiltration
mg	milligram
min	minute
mL	millilitre
mm	millimetre
MPN	most probable number
mPa.s	millipascal second
MVR	mechanical vapour recompression
MWCO	molecular weight cut-off
N	normality
nm	nanometres
OD	osmotic distillation
PA	polyamide
PG	polygalacturonase enzyme
PME	pectinmethylesterase enzyme
PO	peroxidase enzyme
ppb	parts per billion
ppm	parts per million
PS	polysulfone
PTFE	polytetrafluroethylene
PVDF	polyvinylidenefluoride
RO	reverse osmosis
t/d	tonnes per day
TiO_2	titanium oxide
TTF	turbulent thin film
TVE	thermal vacuum evaporation
TVR	thermal vapour recompression

UF	ultrafiltration
wt	weight

CHAPTER 1

1.1. Introduction

Tomatoes are an important commodity and can be consumed either in the fresh state or in processed forms such as juice, paste, ketchup and sauce. The varieties and quality requirements of tomatoes used for processing are different from those required for the fresh market. With fresh market varieties, external characteristics such as colour, size and shape are of greater importance to the consumer than parameters such as sugar content, acidity and total solids content. The end quality of processed tomato products, such as concentrates or pastes, is dependent on the quality of the fresh fruit at the time of processing which in turn is dependent on growth conditions, harvesting and handling techniques (Frenkel and Jen, 1989). The final product quality is also dependent on the processes used to convert the fresh pulp into paste and other concentrated products (Luh and Kean, 1988).

Concentrated tomato products have traditionally been prepared by thermal vacuum evaporation (TVE) processes, which often cause damage to heat sensitive tomato juice components, such as volatile flavour and aroma compounds, as well as inducing undesirable colour changes such as browning. With changes in lifestyle and eating habits, there has been an increase in the demand for tomato products of better sensory quality and attributes such as colour, flavour and texture need to be consistent to retain market share and reputation. Until recently most processors opted for non-visual packaging, such as cans, sachets and opaque plastic packs, for packaging of pastes and concentrates. However, today an increasing number of companies are packing these products in high visual impact glass jars, which creates a traditional feel as well as allowing consumers to view the products prior to purchase. This creates a demand for consistent and high quality products. Consequently, alternative or gentler methods of concentration may be an attractive proposition for improving the quality of existing tomato products or supporting the development of new ones.

Many of the alternative low temperature methods of concentration generally involve the use of membrane processes such as microfiltration (MF),

ultrafiltration (UF), reverse osmosis (RO) and isothermal membrane distillation (IMD). These processes have the capacity to remove water at lower temperatures than TVE processes, thus minimising thermal damage to heat sensitive components and potentially offering a means of preserving the colour, flavour and aroma of tomato products during processing.

Membrane concentration involves the separation of molecules based on their size. The MF process involves the separation of macromolecules larger than 100 nm and is often used for the clarification of fruit juices and wine (Tragardh, 1995). MF is also used for the removal of microorganisms and reduction of bacterial load in products such as milk (Pedersen, 1991). The UF process separates molecules smaller than that achieved by the MF process and in the order of between 0.1 and 100 nm. UF is widely used in the food industry and in particular by the dairy industry for concentrating and fractionating milk/whey proteins (Mohr *et al.*, 1989). The RO process involves the separation of even smaller molecules than is achieved in the UF process, usually between 0.1 and 1.0 nm; hence it is commonly used for the purification of drinking water and seawater. While hydrophilic membrane processes such as MF, UF and RO are well established in the food industry, the use of hydrophobic membrane processes such as IMD are just emerging in food applications.

The IMD process, also known as osmotic distillation (OD), is an Australian patented membrane process exclusively used for the concentration of heat sensitive materials such as pharmaceuticals. The use of IMD in food processing was initially proposed for the concentration of clarified grape juice for winemaking and this research has since been commercialized (Wilson and Peterson, 1992). The current food use of IMD is still essentially limited to the concentration of clarified juices and its use for the concentration of particulate containing juices has not been studied extensively. This study seeks to investigate the potential for using IMD in the concentration of tomato juice, a particulate containing juice, and to develop appropriate processing strategies to enable its use in tomato processing.

1.2. Commercial significance of this investigation

Tomatoes are the second largest fruit crop grown and processed in Australia (Australian Bureau of Statistics, Yearbook 2000). Due to seasonality, tomatoes are harvested only over a few months each year and are processed into a variety of concentrated products. This allows preservation and storage of tomato products over extended periods, hence improving the market availability of such products. In addition, concentration also reduces packaging, transport and storage costs. In Australia, approximately 300,000 tonnes of fresh tomatoes are annually processed into a 28-31°Brix concentrate, with the processed output valued at $175 million (Australian Bureau of Statistics, 2000). The export of concentrated tomato products from Australia has increased steadily over the past five years and is currently worth approximately $14 million per annum.

In Australia, tomato concentrates are currently produced by TVE processes that involve the use of various types of evaporators including falling-film, plate, scraped surface film and centrifugal film evaporators. The traditional evaporators were single stage plants with high-energy requirements (Schwartzberg, 1977), however current evaporation plants consist of at least five stages with three to four effects. Due to the use of multiple stages and effects, most modern tomato paste evaporators utilize thermal vapour recompression or mechanical vapour recompression to reduce steam and energy requirements. Although these modern evaporators are becoming more thermally efficient, they still have drawbacks relating to product quality attributes such as loss of volatile flavour and aroma components and inconsistent product colour (Koseoglu *et al.*, 1991). In order to manufacture concentrates of superior sensory properties that may be attractive for both domestic and export markets, such as Japan and USA, lower temperature processes should be used to preserve the colour, flavour and taste characteristics in the final concentrates.

Alternative lower temperature concentration processes such as MF, UF, RO and IMD, while requiring less energy than TVE processes, can also concentrate without causing drastic changes to the sensory properties of colour, flavour and

aroma in the final concentrates. Other advantages of membrane processing include, lower labor/operating costs (no boiler system required since no steam is used), increased recovery/product yield, lower energy requirements, cold sterilization for cold packing, minimum waste production and possible by-product recovery (Cheryan, 1986).

Currently MF, UF and RO membrane systems are widely used in the food industry for a variety of operations including the concentration of fruit juices, clarification of wine, concentration of starch, fractionation of fermentation liquors, fractionation and demineralization of cheese whey, concentration of enzymes, isolation of bacteria and treatment of water (Cheryan, 1991; Cheryan, 1994; De Carvalho *et al.*, 1998). The use of IMD in the food industry is not widespread and is limited by its present applicability to clarified liquid foods only. However, IMD can potentially concentrate to higher concentration levels than the above membrane processes. This and its ability to be used at ambient temperatures may make it an attractive alternative to TVE for concentrating tomato juice.

This study focuses on the application of IMD in tomato juice processing as it is anticipated that products manufactured using this process may have superior sensory properties, such as color and flavour, to those produced by other processes. It is expected that such products would also have much greater export potential.

1.3. Objectives of this investigation

The general aim of this study has been to investigate the potential for using IMD in tomato processing and particularly in the concentration of tomato juice, a particulate containing juice. As the use of IMD is presently limited to clarified juices, a processing strategy based on fractionation of the tomato juice into serum and solids components followed by concentration of the serum by IMD, either alone or in combination with other membrane processes, and subsequent recombination of the concentrated serum with the original juice solids was adopted.

Furthermore, as minimization of heat damage to the sensory characteristics of the product was of prime importance, other opportunities for reducing the total heat treatment of product have been investigated. Consequently, the thermal break process, a traditional and essential heating process employed in tomato processing to inactivate deteriorative enzymes, was also studied in order to establish the minimal thermal break schedule necessary to effectively inactivate these enzymes.

Thus the specific objectives of the investigation have been to:

1. *Investigate the thermal stability and inactivation characteristics of the three main deteriorative enzymes involved in tomato processing, viz. Peroxidase (PO), Pectinmethylesterase (PME) and Polygalacturonase (PG).*

2. *Identify and evaluate appropriate techniques for the fractionation and clarification of tomato juice into solids and serum components.*

3. *Investigate the use of IMD, either alone or in combination with other membrane processes, for the concentration of tomato juice serum.*

4. *Evaluate the products (tomato pastes) produced by the recombination of IMD concentrated serums with the tomato solids from the fractionation and clarification operations.*

CHAPTER 2

Literature Review - Commercial Processing of Tomatoes

2.1. Introduction

Tomato is a fruit from the Solanaceae (Potato) family. The tomato crop was first domesticated in Mexico but its genetic origin is thought to be the South American coast extending from Ecuador to Peru (Macrae *et al.*, 1993). The genetic placement of tomato is in the Lycopersicon genus which is further subdivided into two species, Eulypersicon and Eriopersicon. The two subspecies are *L.pimpinellifolium* and *L.esculentum.* Eriopersicon has the subspecies *L.cheesmani*, *L.peruvianum*, *L.hirsutum*, *L.chilense*, *L.chmielewskii and L.parviflorum* (Taylor, 1986). Most of these species are rarely grown in Australia even though they have been used in hybridization trials. Commercial interest in Australia is in the *L. esculentum* species which was originally cultivated from the wild variety *L. esculentum* var. *cerasiforme* (cherry tomato). Today hybrid cultivars are genetically bred to improve disease resistance (bacterial speck), tolerance to drought, resistance to insect pests (cutworm and wireworm) and to maximize yield and solids content (Prattley, 1994).

2.1.1. Varietal differences

Tomatoes are the second largest fruit crop grown and processed in Australia (Australian Bureau of Statistics, Yearbook 2000). Fresh salad tomato varieties (field and glass-house) are planted and harvested all year round but processing varieties are affected by climatic conditions and are only harvested over a few months each year. Most of the varieties grown and processed in Australia are Californian varieties that have been genetically bred to suit the Australian climate and growth conditions. Local processing crops include varieties such as UC82B, Alta, Pacesetter, Hypeel 696 and several Heinz owned varieties. Most of these processing varieties are planted in September and harvested between February and April of the following year. Districts within Australia that offer suitable growth conditions include areas such as Boort, Corop, Rochester, Undera, and Tatura in Victoria and Finley, Leeton and Cowra in New South Wales.

2.1.2. External appearance and quality

Quite often the internal sensory quality is judged by the external appearance of tomato fruits. Most of the selected growth conditions used during the domestic cultivation of tomatoes are often compromised for commercial crop production. Commercial tomato crops are selectively different to domestic crops because they are bred to maximize product yield as well as product quality (Frenkel and Jen, 1989). Characteristically the size, colour, shape and texture determine the external appearance of mature tomato fruits and these characteristics are frequently used as indicators of quality.

2.1.2.1. Size

Consumers often associate smaller fruit size with better taste and flavour. The smaller cherry tomato is often preferred in salads because of its superior flavour than the larger fruit varieties. In Australia there are no standards established for tomato fruit size hence most companies resort to the use of standards out-lined by the United States Department of Agriculture (USDA).

2.1.2.2. Shape

The tomato fruit has two basic shapes, the round plum type and the elongated pear type. The round-shaped tomato is more popularly used for the preparation of salads as compared to the elongated Roma tomato, which is generally used for canning and processing into sauce, paste and concentrates.

2.1.2.3. Colour

Often colour indicates the ripeness and the eating quality of a fruit. The colour of processed tomato is as important in the finished product as it is in the fresh fruit because consumers often associate better eating quality with better colour. The redness of tomatoes is mainly due to the carotenoid, lycopene (Khachick *et al.*, 1998). Other major carotenoids found in tomatoes are phytoene, phytofluene, β-carotene and γ-carotene (Davies and Hobson, 1981). In the early stages of fruit development, carotenoid compounds are masked by chlorophyll and generally increase on the onset of chlorophyll degradation, which is responsible for initiating the ripening process of fruits (Wills *et al.*, 1998). In recent years the

lycopene from tomatoes has been isolated and used as a natural red pigment/food colorant (Nir *et al.*, 1994). Consumption of lycopene-rich tomato products is also reported as reducing the risk of some cancers (Giovannucci *et al.*, 1995; Narisawa *et al.*, 1996). As yet there have been no standards established for colour grading of tomato products in Australia, however individual processors have created in-house standards as a guideline for assessing the final quality of processed tomato products.

2.1.3. Composition

The composition of tomato can vary within the season, within the same growing district and even within the same cultivar (Davies and Hobson, 1981). Tomatoes are composed of a complex mixture of constituents and a simple diagrammatic representation of tomato composition is given in Figure 2.1 (Stevens, 1985). The internal constituents such as sugars, acids, pectins, polysaccharides and volatile flavors contribute to the unique sensory attributes of flavour and aroma of tomato products.

These tomato constituents are often monitored throughout growth, ripening and processing stages and reflect the conditions of that season. For example, climatic conditions such as high rainfall and water shortages can affect the composition of tomatoes and Stevens (1985) reported that low water tensions and availability during growth and ripening stages could result in tomato fruits of lower acid and sugar content. Lower acid content of tomato fruits can cause some processing problems such as reduced microbiological stability of intermediate and final processed tomato products. If the desired acidity is not achieved during the growth and ripening stages, the tomato juice is usually acidified during the early processing stages so that the final concentrate has the required level of acidity to prevent microbial and mould growth.

2.1.3.1. Flavour

The flavour is usually the most dominant sensory feature in processed tomato products. The variation in flavour is determined by the sugar content and acidity

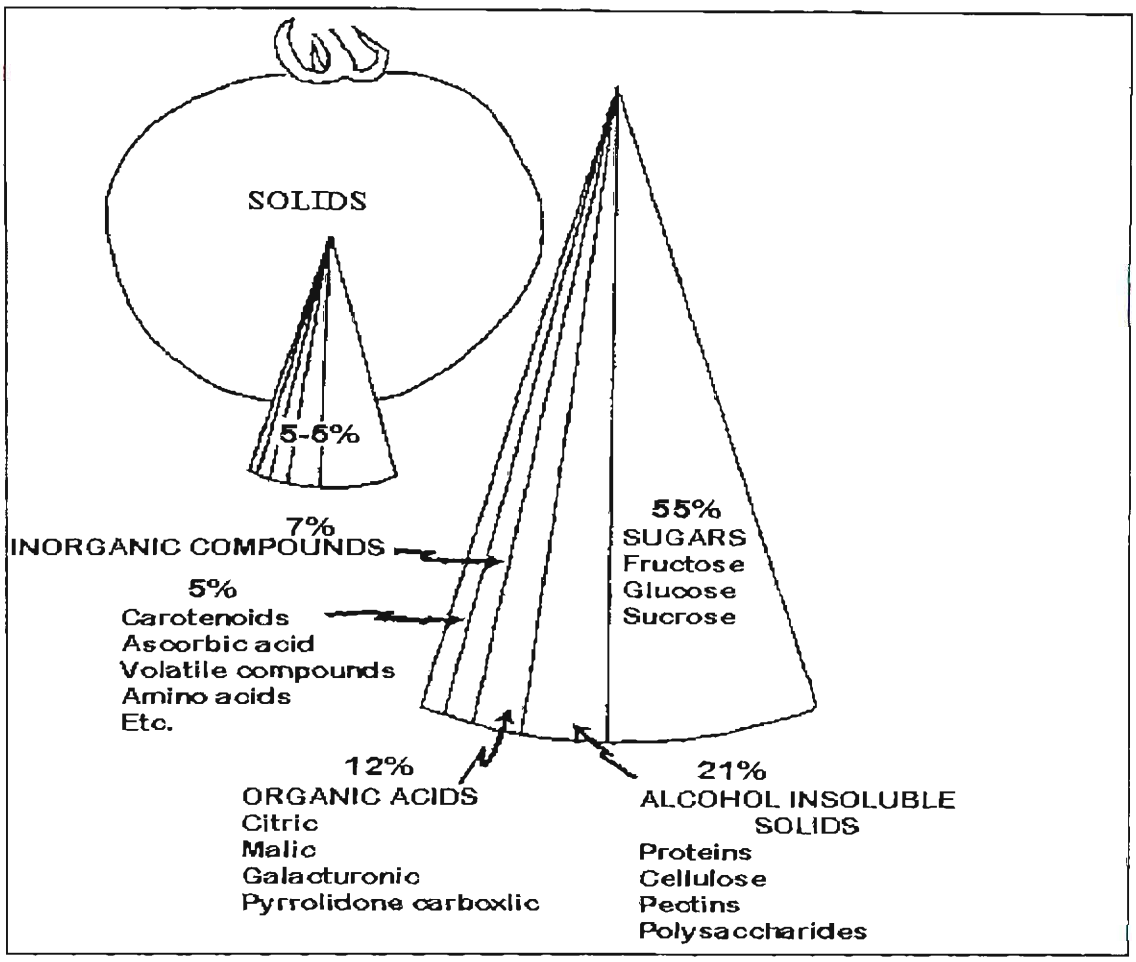


Figure 2.1 Composition of tomato (Stevens, 1985)

level (Redenbaugh *et al.*, 1992), as well as by the volatile components of the tomatoes (Buttery *et al.*, 1990*a*). The two principal sugars, fructose and glucose, constitute approximately half of the soluble solids content of tomatoes (Hayes *et al.*, 1998) and the two major organic acids found in tomatoes are citric and malic. The volatile components of tomatoes, often too complex to fully categorize, can be classified into three major groups, viz. aliphatic compounds, terpenoids and aromatic heterocyclic compounds (Buttery *et al.*, 1990*a*). The volatile components are directly affected by thermal processes and Poretta *et al.* (1992) concluded that the formation of additional volatile compounds, such as hydroxymethylfurfural (HMF), was higher in tomato pastes made by the 'hot break' processes than those made by the 'cold' break processes. HMF is a browning compound formed when reducing sugars are heated in an acidic medium (Porretta and Sandei, 1990). Research also suggests that the volatile

component of tomatoes is related to the carotenoid content and that carotenoids may be precursors of these volatile compounds (Stevens, 1985).

The overall flavour of fresh and processed tomatoes is influenced by a combination of factors including varietal differences (Daood *et al.*, 1990), titratable acidity (Stevens, 1985), growth conditions (Johansson *et al.*, 1999; Hayes *et al.*, 1998), post-harvest storage conditions (Mohammed *et al.*, 1996) and stage of ripeness (Davies and Hobson, 1981). The extent and duration of thermal processing can also contribute to the overall acceptance of flavour and other sensory attributes of processed and concentrated tomato products. For preservation of colour and flavour, low temperature concentration methods such as membrane processing may be more suitable than conventional thermal vacuum evaporation methods.

2.1.3.2. Texture

The texture of tomatoes is as important in the production process as it is during the harvesting stage. The pericarp of the fruit has to be firm enough to withstand mechanical injury during harvesting, storage and subsequent processing. Damage to the pericarp can initiate the action of pectolytic enzymes such as pectinmethylesterase (PME) and polygalacturonase (PG), which in turn can affect the final viscosity of processed concentrates and pastes. The texture of tomato is influenced by the balance of constituents such as cellulose, hemicellulose, pectic substances and cell wall proteins (Frenkel and Jen, 1989). Changes in texture during ripening, softening and rotting processes is generally caused by deteriorative enzymes such as PME and PG (Klein, 1992). The texture of processed tomato products can be determined analytically by either viscosity or consistency measurements. The Bostwick consistency test is the most common method of determining the acceptability of the texture of tomato pastes and concentrates (Hayes *et al.*, 1998).

2.1.3.3. Nutritional Quality

The nutritional composition of raw tomatoes is very similar to other high moisture fruits and vegetables. The chemical composition and hence the nutritional value

of raw tomatoes and tomato juice is essentially the same (Nelson and Tressler, 1980). The vitamins are often considered to be the most important component in terms of nutritional value. Raw tomatoes contain a good balance of vitamins and minerals, in particular vitamins A and C (Vit A content of 0.19-1.67 mg/100g and Vit C content of 8.40-59.0 mg/100g) (Redenbaugh *et al.*, 1992). The vitamin C content of tomatoes is higher than in most fruits and vegetables except for potatoes and citrus fruits (Frenkel and Jen, 1989). The vitamin content of tomatoes is dependent on the genetic origin, environmental factors, geographical location and post-harvest handling techniques (Davies and Hobson, 1981).

2.2. Production of tomatoes in Australia

The total production, the land area used for production, the annual yield and the total gross value of the fresh tomato crop produced in Australia is assessed and documented every four years and the data for the four year period from 1996 to 2000 is presented in Table 2.1. The production, value and yield of fresh tomatoes in Australia has risen steadily over the four year period except for 1997 when the production was marginally down by 3%. The slight decline in the production figure was responsible for lowering the gross value by 5% from the previous 1996 period. The land area used for the tomato crop cultivation during the four-year period has not changed significantly and having a range between 8 and 9 kilo hectares. However, the total yield per hectare obtained has increased steadily over this period, increasing by around 5-7% per annum. This is due to better crop management during growth and improvement in the harvesting techniques as well as the use of higher yielding varieties.

Data on the total production, land area used, yield and gross value of fresh tomatoes grown in each state is only collected every four years and the latest data (1999-2000) is presented in Table 2.2. In Australia, tomatoes are grown and processed mainly in Victoria (Vic), New South Wales (NSW) and Queensland (Qld). Other Australian states such as the Australian Capital Territory (ACT), South Australia (SA), Western Australia (WA), Tasmania (Tas) and the Northern Territory (NT) only have low production of tomatoes. Victoria had the highest

production, accounting for 60% of the national harvest while Queensland had the highest crop value, accounting for 56% of the total crop value of fresh tomatoes harvested in Australia. The higher crop value in Queensland is associated with much of their crop going to the fresh produce market rather than processing, as well as the supply of fresh tomatoes to other states of Australia during their non-seasonal period.

Table 2.1 Production, land usage, yield and gross value of fresh tomato production in Australia during the period 1996-2000

	1996-1997	1997-1998	1998-1999	1999-2000
Production (kt)	393	380	394	414
Area (kha)	9	8	9	8
Yield (t/ha)	44.5	47.4	46.1	49.7
Gross value ($m)	177	173	192	190

Source: Australian Bureau of Statistics, Year Books Australia 1996 and 2001

Table 2.2 The production and total gross value of fresh tomatoes in the different states of Australia for the year ending 1999-2000

	NSW	VIC	QLD	SA	WA	TAS	NT	ACT
Production (kt)	60.3	249.3	87.9	2.4	12.0	0.9	0.3	0.4
Area (kha)	1.2	3.4	3.3	0.1	0.3	<0.1	<0.1	<0.1
Yield (t/ha)	50.3	73.3	26.6	24.0	40.0	63.2	206.7	111.5
Gross value ($m)	9.7	58.5	107.2	3.9	11.0	1.3	-	0.1

Source: Australian Bureau of Statistics, 1999-2000.

2.3. Consumption of tomatoes in Australia

Tomatoes can be consumed as a fresh product or as a processed commodity in the form of canned tomatoes (whole or pieces), paste, pulp, puree or sauce. In Australia, approximately 85% of the fresh tomato crop is processed into tomato paste and concentrates. These pastes and concentrates become the basis for the preparation of many other tomato products such as juices, soups and sauces. Table 2.3 summarises the quantity of tomatoes available for consumption, the

apparent per capita consumption and the value of the consumption of fresh tomatoes in Australia during the last documented four-year period.

The availability, per capita consumption and total gross value of tomato consumption in Australia have risen steadily over the four-year period except in 1997-1998 when the availability declined by 23%. Although the per capita consumption showed little change, the gross value increased by 10% in the 1995-1999 period. The consumption trend also reflects the import data that is discussed further in Section 2.4.

Table 2.3 Availability, apparent per capita consumption and gross value of tomatoes in Australia during the 1996-2000 period

	1995-1996	1996-1997	1997-1998	1998-1999
Availability (t)	433,913	477,800	389,648	469,032
Per capita consumption (kg)	23.8	25.9	20.9	24.9
Gross value ($m)	176	177	173	192

Source: Australian Bureau of Statistics, Yearbooks, 2000-2001.

2.4. Exports and imports of tomato products

The quantity and value of tomato products exported from Australia in the documented five-year period (1996-2001) has increased by 51% and 63% respectively as compared to the quantity and value of tomato products imported during the same period, which has only increased by 20% and 30% respectively (Tables 2.4 and 2.5). The total quantity and value of imports of tomato products into Australia still outweighs the total quantity and value of tomato products exported by Australia. The main export destinations include Hong Kong, Indonesia, Japan, Malaysia, New Zealand and the Pacific Islands. In 1996, the major products exported by Australia included preserved tomatoes (whole or pieces), tomato puree/paste and tomato sauce. In the last 5 years there has been significant changes in the quantities of these products exported by Australia. The quantity of preserved tomato products exported decreased by 80% while the

quantity of tomato sauce exported increased by the same percentage in this documented five-year period.

Table 2.5 shows that the quantity and value of imported processed tomato products into Australia increased steadily over the five years, with the quantity increasing from 34,468 tonnes in 1996 to 42,288 tonnes in 2001 and the value increasing from $32.5 million in 1996 to $46 million in 2001. The origins of these processed tomato products include countries such as China, Greece, Italy, New Zealand, Spain, Thailand, Turkey and the USA. Canned tomatoes, either whole or in pieces, is the most common product imported. Although the quantity of canned tomato whole/pieces has not changed dramatically, the quantity of other tomato products such as tomato sauce and tomato paste/puree has changed significantly. In the last five years the quantity of tomato sauce imported into Australia has almost doubled and the quantity of paste/puree <1.14 L has also increased by 80%. There were also increases in the quantity of paste/puree >1.14 L (30%) and whole/ pieces <1.14 L (9%) imported into Australia.

The increased export and import of tomato sauce and tomato paste/puree shows that eating habits here in Australia and the countries of export have changed dramatically in the last 5 years. The change in export-import trends may be due to the increased production and yield of fresh tomatoes in Australia. The increase in export-import quantities shows that Australia has a flourishing tomato processing industry and processed tomato products are still in demand.

Table 2.4 The total quantity (tonnes) and value ($m) of tomato products exported by Australia during the period 1996-2001

	1996-1997		1997-1998		1998-1999		1999-2000		2000-2001	
	tonnes	$m	tonnes	$m	tonnes	$m	tonnes	$m	tonnes	$m
Tomatoes (preserved)	1,056	1.36	370	0.77	515	0.77	936	1.19	242	0.66
Tomatoes (unpreserved)	15	0.09	31	0.23	40	0.22	*		*	
Tomato puree or paste (solids > 7%)	1,055	1.48	4,420	4.70	9,156	10.70	3,884	5.33	1,315	2.75
Tomato sauces	1,065	2.25	2,387	6.33	1,395	4.38	3,972	9.28	4,766	10.52
Total	3,246	5.18	7,208	12.03	7,208	16.07	8,792	15.80	6,323	13.93

Source: Data from exports embargo, Australian Bureau of Statistics, 2002.
*Reported data was combined with tomato puree or paste data for years 1999-2001
Preserved - tomatoes preserved by either vinegar or acetic acid.
Unpreserved - all tomatoes excluding those preserved by vinegar or acetic acid.

Table 2.5 The total quantity (tonnes) and value ($m) of imports of tomato products into Australia for the period 1996-2001

	1996-1997		1997-1998		1998-1999		1999-2000		2000-2001	
	tonnes	$m	tonnes	$m	tonnes	$m	tonnes	$m	tonnes	$m
Whole peeled/pieces < 1.14 L	12,380	10.55	15,255	14.27	15,225	17.81	15,719	15.97	13,777	14.63
Whole peeled/pieces > 1.14 L	10,380	7.97	8,771	7.47	8,262	8.26	8,475	7.43	7,742	7.58
Dried whole/pieces	525	0.33	228	0.26	173	0.18	*		*	
Paste, pulp, puree <1.14 L	1,127	1.47	3,745	4.14	2,104	2.27	3,408	3.40	6,070	4.91
Paste, pulp, puree >1.14 L	6,377	6.48	3,911	3.76	1,994	2.23	11,815	12.34	8,955	9.42
Sauce	3,679	5.70	4,067	6.69	7,789	10.17	5,386	7.71	5,744	9.45
Total	34,468	32.50	35,977	36.59	35,543	40.92	44,803	46.85	42,288	45.99

Source: Data from imports embargo, Australian Bureau of Statistics, 2002

*Reported data was combined with whole/pieces, volume > 1.14 L and volume < 1.14 L for years 1999-2001

> 1.14L - volume exceeding 1.14 litres

< 1.14L - volume less than 1.14 litres

2.5. Australian standards for tomato processing

Standards and specifications are generally used to ensure product uniformity and quality. In Australia, due to the absence of formal standards for tomatoes and tomato products, tomato processors have taken the liberty of specifying in-house standards so those individual products can be monitored during processing and subsequent storage. These industry standards are based mainly on the United States Department of Agriculture (USDA) guidelines since there are no standards for tomato products in the Food Standards Australia New Zealand (FSANZ) new Food Standards Code. The testing parameters used to monitor quality during tomato processing involve the measurement of pH, titratable acidity, colour, consistency and flavour of tomato products. The most important microbiological testing parameter involves the measurement of the Howard Mould Count.

To the consumer, an accepted colour of tomato paste and puree is bright red and free from black specks, insects and other foreign matter (Ranken and Kill, 1993). In order to achieve uniformity during processing, tomato paste colour can be measured instrumentally by a Munsell spinning disk colorimeter, a Tristimulus colour meter, a reflectance spectrophotometer or a Lovibond tintometer. Although most of these instruments are still widely used, some limitations apply for the Munsell and Lovibond systems since they are based on the judgment of the human eye (Hayes *et al.*, 1998). The chromameter is the most common instrument used in Australia for the measurement of colour and is based on the original Tristimulus colour meter. The chromameter uses the Hunter-Gardner system of classification and three common coordinates L*, a* and b* values are used to describe colour. The L* value reports the lightness or luminescence factor, a positive a* value describes redness, a negative a* value describes greenness, a positive b* value describes yellowness and a negative b* value describes blueness. The a/b ratio describes the overall redness relative to other colours. Although there are no guidelines for an acceptable colour of tomato pastes in Australia, companies have set internal colour standards of an a*/b* ratio of 1.90 as being a first grade paste or puree and a 1.80 ratio as being a second grade product (Hayes *et al.*, 1998). Australian companies have significantly lower

colour standards in comparison to some overseas countries where a higher a*/b* ratio of 2.3 is more acceptable for a first grade tomato paste (Brimelow, 1987; Kent and Porretta, 1990).

The flavour of processed tomato is as important as any other sensory property, however most companies do not routinely test for acceptability of flavour. This may be due to the complexity of the assessment since raw tomatoes can contain more than 400 different flavour compounds (Buttery *et al.*, 1990*a*).

Consistency of tomato paste is important since most consumers associate quality with consistency. The Bostwick Consistometer measures the distance of tomato paste flow under its own weight during a given time. The length of flow is a measure of the consistency of the paste. The Bostwick Consistometer has been widely used both overseas and in Australia to measure consistency despite the limitations that the sample has to be diluted prior to assessment (Hayes *et al.*, 1998). Although there are no standards for consistency in the ANZFA or USDA guidelines, most companies have created internal standards and routinely assess the consistency of tomato products. An acceptable standard for Bostwick consistency for first grade tomato paste is that the flow should be less than 14 cm in 30 sec at 20°C (Hayes *et al.*, 1998).

The acceptable Industry standard for the Howard Mould Count requires an absence in more than 50% of the microscopic fields examined for tomato paste or puree products. However, some Australian companies, for export purposes, have set a standard requiring absence in more than 60% of the microscopic fields examined. This allows a safety margin for export products as well as allowing pastes of higher mould counts to be reworked or diluted to meet the regular industry standard (Heinz Watties Australasia, 1999).

2.6. Tomato processing

The demand for concentrates with improved sensory properties such as colour, flavour and texture has increased during the last ten years and as a consequence has significantly changed tomato processing operations (Porretta and Poli, 1997; Porretta *et al.*, 1992). New processing techniques such as the use of lower break temperatures (Laratta *et al.*, 1995), high pressure for enzyme inactivation (Cano *et al.*, 1997), microwave processes for enzyme inactivation (Porretta and Leoni, 1990) and ultrafiltration for concentration are some of the techniques that have been introduced to improve sensory attributes. Typical tomato products processed domestically include canned whole tomatoes, pulp, paste, sauce and juice. Figure 2.2 illustrates the unit processes used during the manufacture of different tomato products. The process for tomato sauce is not shown since it is generally prepared from concentrated tomato pulp. Since some confusion can arise from the terms pulp, puree, paste and juice the following definitions describe the different products (Hayes *et al.*, 1998):

Tomato pulp refers to crushed tomato before or after removal of the seeds and skin.

Tomato puree term used to describe lower concentrations of tomato paste (8-24% NTSS-natural tomato soluble solids).

Tomato paste refers to the product obtained after the seeds and skin have been removed and the pulp has been concentrated to at least 24% NTSS.

Tomato juice refers to the liquid from crushed tomato that has had the seeds and skin removed, has been subjected to fine screening and is intended to be consumed without concentration or dilution.

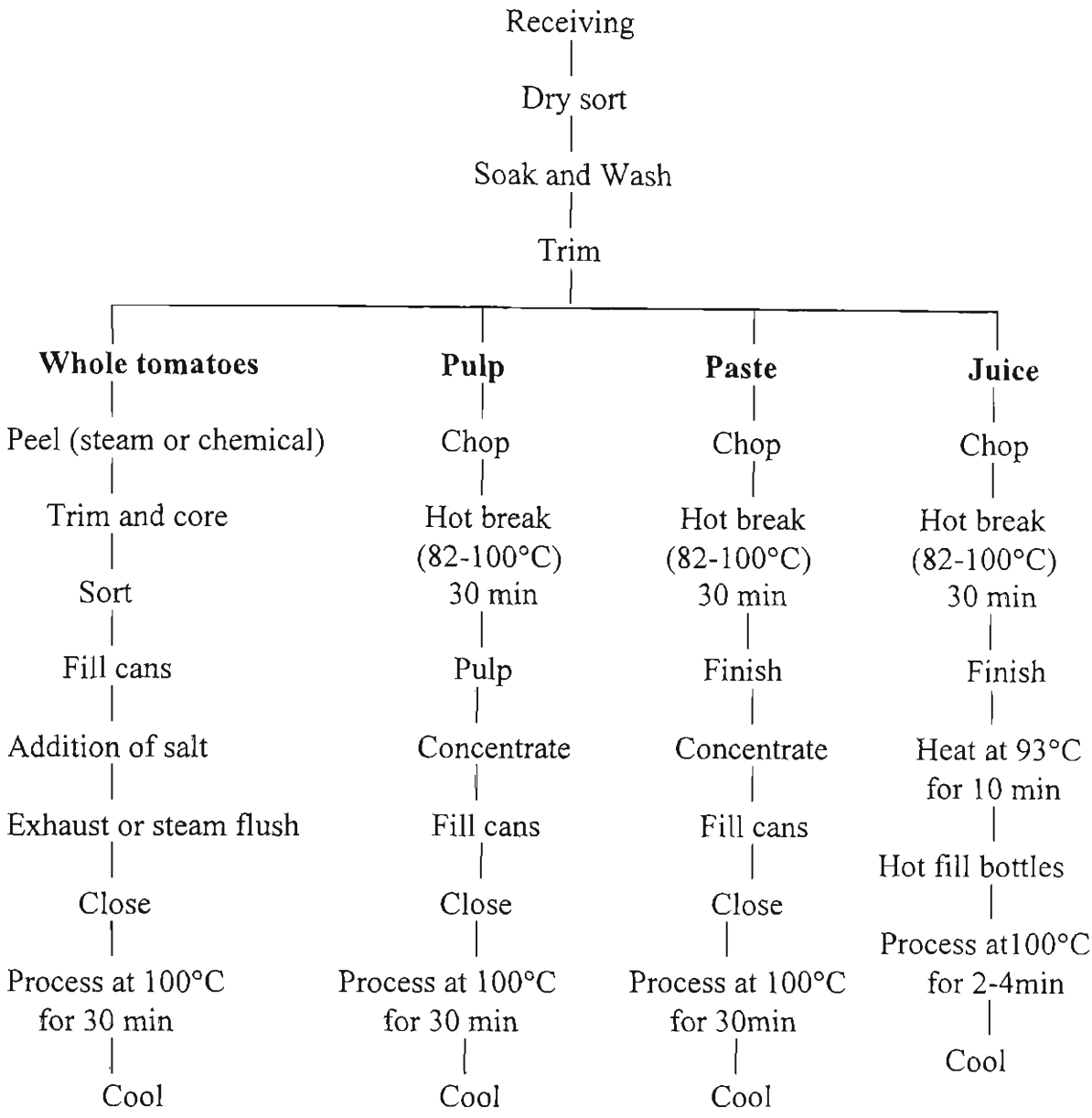


Figure 2.2 Unit operations involved in tomato processing (Adapted from Luh and Kean, 1988; Redenbaugh *et al.*, 1992).

2.6.1. Unit operations involved in tomato concentrate preparation

In Australia tomatoes are processed into concentrates to reduce storage and transportation costs and increase availability of products out of season. According to the ANZFA Food Standards Code, tomato pastes must contain at least 21% total solids on a salt-free basis. Tomato concentrates are usually concentrated using TVE processes. Figure 2.3 shows the basic unit processes used for the manufacture of tomato concentrates.

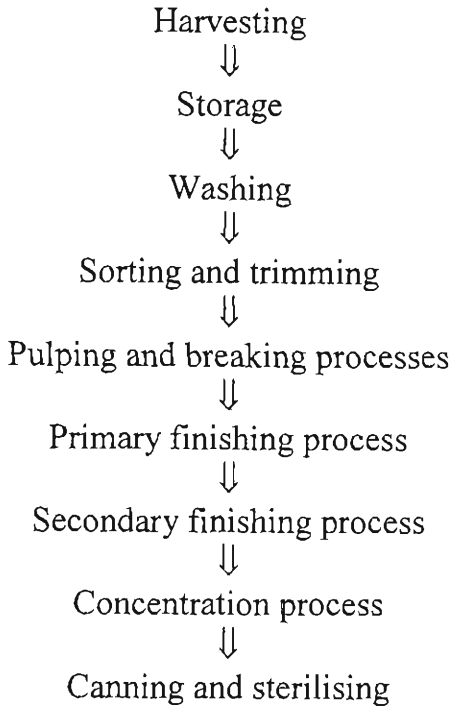


Figure 2.3 Unit processes used for manufacture of tomato concentrates.

2.6.1.1. Harvesting and storage processes

In Australia tomatoes are harvested and processed between February and April. Usually tomatoes used for the fresh trade purposes are hand-harvested whereas tomatoes destined for commercial processing are machine-harvested due to economic reasons. Fruit cultivars used for mechanical harvesting usually have high yields, small vines and concentrated maturity (Prattley, 1994). Processing fruit varieties also detach easily from the vine and are able to withstand minor physical damage caused by the mechanical harvester. A mechanical harvester during operation is shown in Figure 2.4 and in detail in Figure 2.5. The indices used to determine suitability for harvesting are the total solids content and the pH level or titratable acidity content. Harvested fruits are stored in wooden bins (0.5-1 tonne capacity) at room temperature (20°C) and the bins are regularly washed to avoid cross-contamination. Since chilled storage is expensive and exposure to high storage temperatures can affect post-harvest quality (Mohammed *et al.*, 1996), the mechanically harvested tomatoes are processed within 48 hours to avoid chemical and microbiological deterioration prior to processing. A storage

temperature of 12°C for a maximum of 3 to 4 days is recommended for harvested fruits.

2.6.1.2. Washing process

The washing of tomatoes is generally done before the sorting process because mould and rot removal is easier in washed vegetables. A microbial inhibitor (chlorine at 5-10 ppm) is added to the wash water to prevent cross-contamination (Luh and Kean, 1988). The most common type of washing device is the rotary washer (spray-roller) which is effective for both soil and mould removal. The water from the washer is recycled and the silt is drained to waste containers.

2.6.1.3. Sorting and trimming processes

Sorting involves the removal of decayed fruits and stalks. Several types of sorting systems are used including table, simple apron and divided apron types. The more modern type of system consists of an incline inspection conveyor belt, which enables the fruits to be turned during inspection (Figure 2.6). This allows all parts of the fruit to be inspected before primary processing commences.

Figure 2.4 Mechanical harvesting of tomatoes (Leoni, 1993)

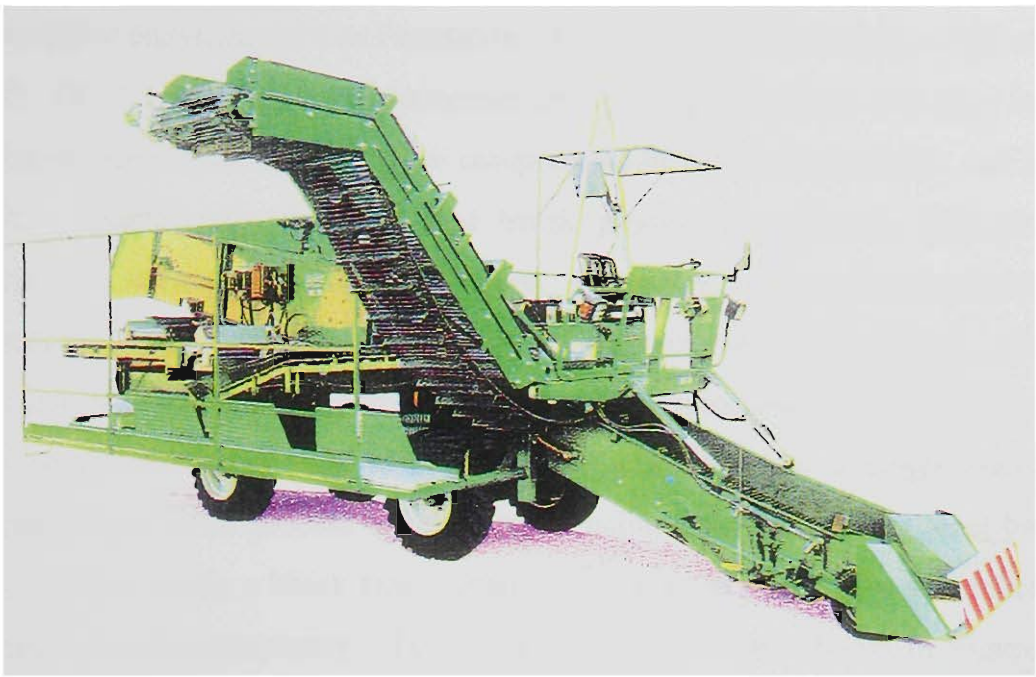


Figure 2.5 A typical mechanical harvester (Leoni, 1993)

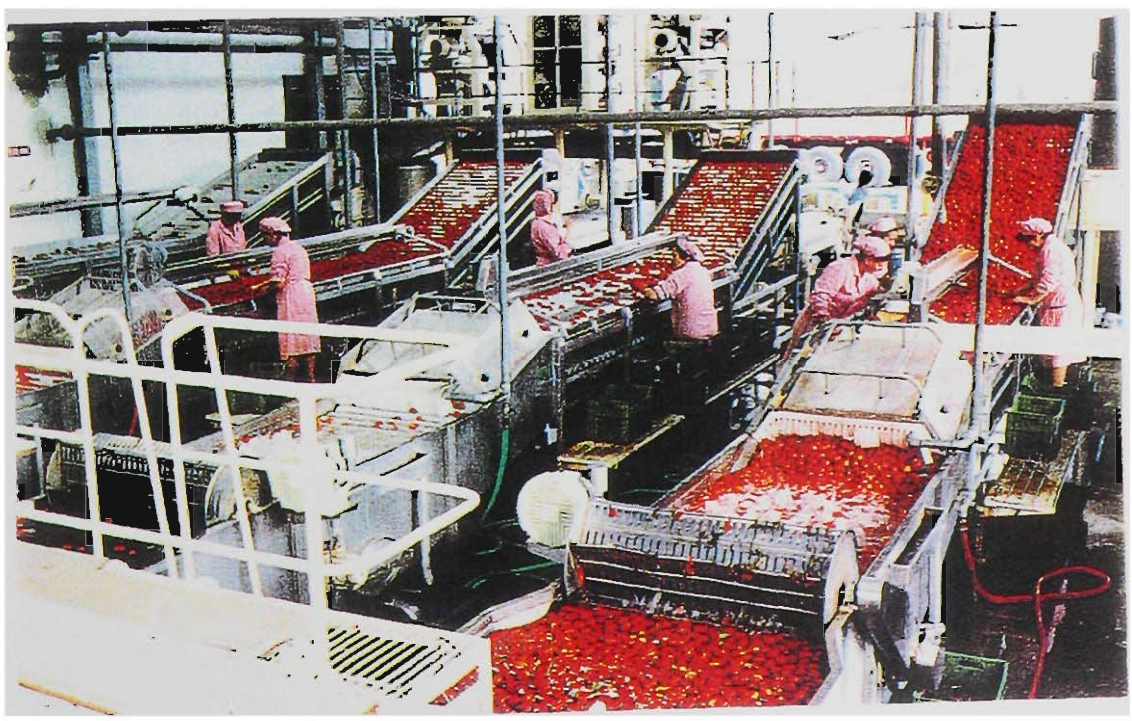


Figure 2.6 Washing and sorting tomatoes (Leoni, 1993)

2.6.1.4. Pulping and break processes

An initial heat treatment, called the 'break process,' is used to inactivate deteriorative enzymes such as Peroxidase (PO; EC 1.11.1.7), Pectinmethylesterase (PME; EC 3.1.1.11) and Polygalacturonase (PG; EC 3.2.1.5) and also release maximum juice from the cellulose components of the tomatoes (Luh and Kean, 1988). Traditionally the pulp and break processes were two separate unit processes, however the delay between these two processes permitted the spontaneous activity of deteriorative pectolytic enzymes such as PME and PG. The activity of PME and PG adversely affected the juice viscosity and yield hence most companies today tend to combine the processes into a single operation. Nowadays the break process is achieved by using rotating stainless steel heating coils, housed within a break tank, which disintegrate the tomatoes and inactivate the enzymes simultaneously. Typical hot break tanks are shown in Figure 2.7. The tomatoes are macerated at 95°C and held in the tank for approximately 30 minutes. The disintegrated pulp is separated from seeds, skins and cellulosic material by finishing devices (see Sections 2.6.1.5 and 2.6.1.6).

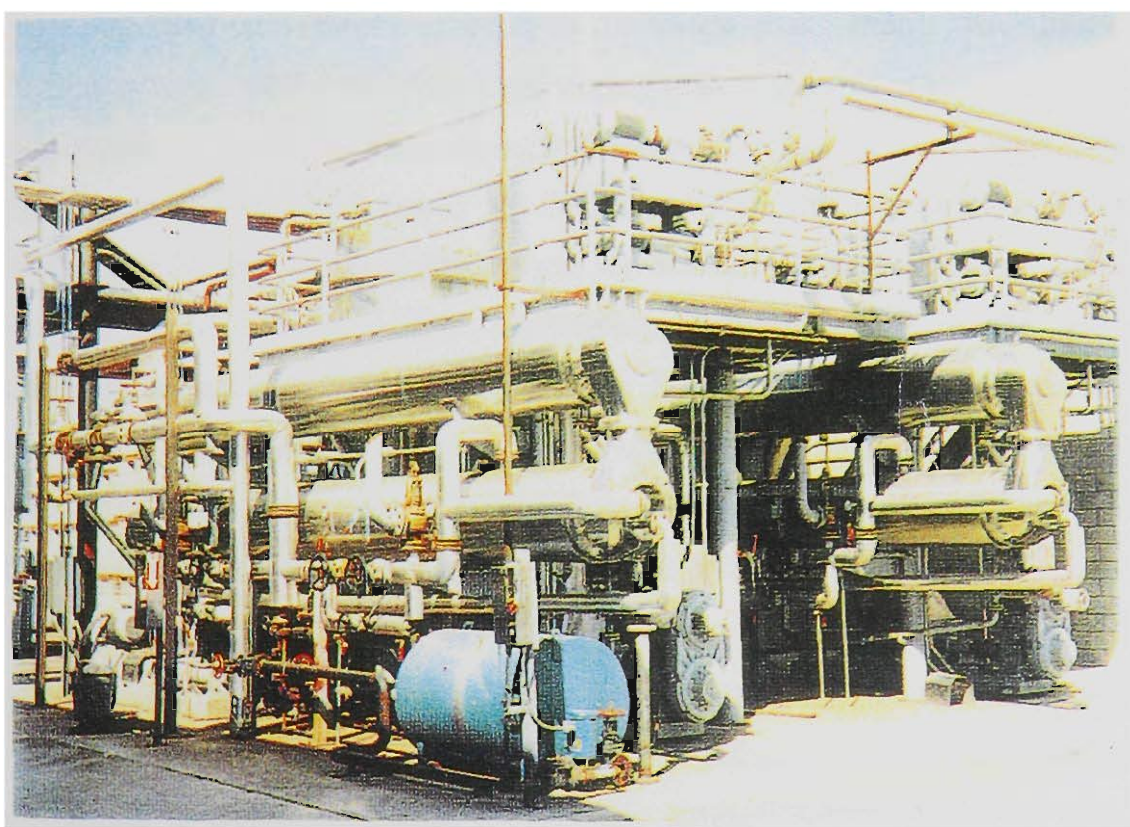


Figure 2.7 Hot break tanks for enzyme inactivation in tomatoes (Leoni, 1993)

Break processes can be classified as cold, medium or hot and the chosen process is usually dependent on the quality of the final product desired. Cold break processes are achieved at temperatures in a range of 60°C and 65°C. Medium break processes usually involve temperatures in a range between 80°C and 85°C and hot break processes are usually achieved at 95°C. The type and the duration of the break process directly affect the pectin retention in the juice and contribute to the final viscosity of the tomato concentrates (Caradec and Nelson, 1985; Xu *et al.*, 1986). The temperature and duration of the break process used in industry is often the same for every batch regardless of the tomato variety, size and composition. The enzymes of major concern during tomato processing are PO, PME and PG and break processes should be designed to ensure their inactivation.

PO enzyme is associated with ripening and senescence in fruits and vegetables (Klein, 1992). However, after harvesting PO can cause deteriorative changes in flavour, colour and texture in fruits and vegetables (Cano *et al.*, 1995; Robinson, 1991). It is considered to be the most heat stable enzyme in fruits and vegetables (Baardseth and Slinde, 1987) and for this reason is often used as an index of blanching efficiency (Brewer *et al.*, 1994; Williams *et al.*, 1986). The ability of PO to regenerate after inactivation and during chilled and frozen storage is also a major concern in the food processing industries (Ganthavorn and Powers, 1988; Hemeda and Klein, 1991; Lopez and Burgos, 1995). This regenerative property of PO may be due to the different heat sensitivities of the isoenzymes present (Forsyth *et al.*, 1999). Other inactivation techniques such as the use of antioxidants and manothermosonication for PO inactivation have shown some promise (Hemeda and Klein, 1991; Lopez and Burgos, 1995). However, further trials need to be carried out to establish the positive effects of such treatments. The peroxidatic reaction can be expressed by the following equation:

$$ROOH + AH_2 \rightarrow H_2O + ROH + A$$

where R can be a hydrogen ion (H^+), a methyl group (CH_3) or an ethyl group (C_2H_5); AH_2 is the hydrogen donor and A is the oxidized donor. Compounds such as phenols (p-cresol and guaiacol), aromatic amines (aniline, benzidine and o-

dianisidine) and reduced nicotinamide-adenine dinulcleotide are typical hydrogen donors that are oxidized during the reaction (Klein, 1992).

The pectic enzymes PME and PG play an important role in the ripening and softening of tomato fruit tissue during development due to their action on pectic substances (Gross, 1990; Hobson and Grierson, 1993). Pectic substances are carbohydrate polymers consisting of α-1,4-linked D-galacturonic acid units with sections of L-rhamose-rich regions with side chains consisting of arabinose, galactose and xylose (Pilnik and Rombouts, 1981). The higher pectic substances are located in the middle lamella and the primary cell wall of plants (Pilnik and Voragen, 1991). During post-harvest storage PME hydrolyses methyl esters of the high methoxyl pectin molecules and reduces them to low methoxyl pectin molecules. This causes clarification and cloud loss in fruit juices prepared from stored produce. The action of PME enzyme is complementary to that of the PG enzyme which hydrolyses the glycosidic bonds of the reduced pectin molecule and hence decreases the viscosity of the juice. The classification of pectic enzymes is based on their reactions (Wong, 1995) and the following describes the reactions of PME and PG:

1. PME hydrolyses the methyl ester groups by deesterification of the pectin molecule. It acts on the methyl ester group of a galacturonate unit next to a nonesterified galacturonate unit.
2. PG hydrolyses the α-1,4-glycosidic bonds. The exo-PG (EC 3.2.1.67) cleaves bonds from the nonreducing end while the endo-PG (EC 3.2.1.15) attacks the glycosidic bonds randomly.
3. Pectate Lyase (PEL) enzyme acts by cleavage of nonesterified galacturonate units via β-elimination. Both endo and exo-PEL prefer pectate and low-methoxyl pectin as substrates.
4. Pectin Lyases (PNL) are all endo-enzymes and only act on esterified galacturonate units by β-elimination.

The specific demethoxylation of the methyl esters in pectin by the PME enzyme is a prerequisite for the hydrolysis reaction of pectins by the PG enzyme (Labib and El Ashwah, 1995; Pressey and Avants, 1982). The unique mode of action of PME and PG enzymes is illustrated by the reactions shown in Figure 2.8. The methanol produced from the PME reaction can be determined chromatographically (McFeeters and Armstrong, 1984), colorimetrically (Cameron *et al.*, 1992) spectrophotometrically (Marangoni *et al.*, 1995) or titrimetrically (Laratta *et al.*, 1995; De Sio *et al.*, 1995; Wicker, 1992).

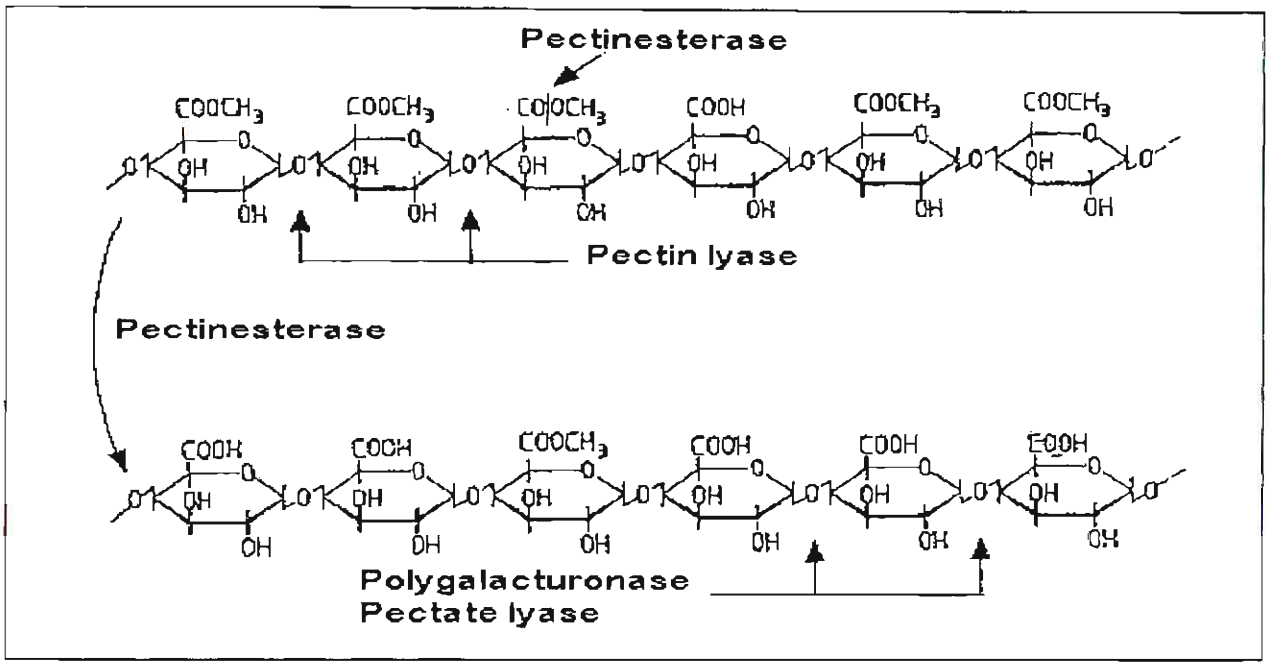


Figure 2.8 The mode of action of PME and PG enzymes (Rombouts and Pilnik, 1978)

PG is the major pectic enzyme associated with the ripening and softening of fruit and vegetable tissue (Barrett and Gonzalez, 1994). PG is present at very low levels in mature green fruits but increases markedly as fruits change colours (Brady *et al.*, 1982). Two isoenzymes of PG have been extracted from tomatoes, PG1 and PG2 (Wong, 1995). PG1 can be differentiated from PG2 because it has a higher molecular weight and is more heat stable than PG2. The PG 2 isoenzyme appears later in the ripening process and becomes the major enzyme in the ripening process (Brady *et al.*, 1982). PG, unlike most enzymes, reacts at an

acidic pH of 4.5 and only reacts on the reduced pectin substrate, hence relying completely on the activity of the native PME enzyme to provide substrate for its action.

2.6.1.5. Primary finishing process

The purpose of the finishing process is to remove seeds, skins and cellulosic material from the juice component. The primary finisher or juice extractor is sometimes called a "pulper" by tomato processors. Common primary juice extractors are mainly screw type devices that have screen sizes between 2.3 and 3.0 mm (Figure 2.9). This primary extractor draws in air, which is used to exert pressure on the pulp against the screen. The air pressure can be controlled by a helical screw and the higher the air pressure the greater the volume of juice extracted. Approximately three percent of waste (seeds and skin) is removed from the juice at this stage and is usually discarded or used for cattle feed.

2.6.1.6. Secondary finishing process

Secondary juice extractors are usually paddle type devices with screen sizes ranging between 0.5 and 1.2 mm. The screen size is important during secondary finishing since the particle sizes obtained in the juice at this stage affects the consistency of the final tomato paste (Tanglertpaibul and Rao, 1987). The screen is fitted around the horizontal rotating paddle, which rotates in a clockwise direction forcing the juice through the screen (Figures 2.10 and 2.11). After the finishing process, the pH of the juice is checked and adjusted to pH 4.2-4.3 by the addition of citric acid if required. The finished tomato juice is then concentrated to the required soluble solids level.

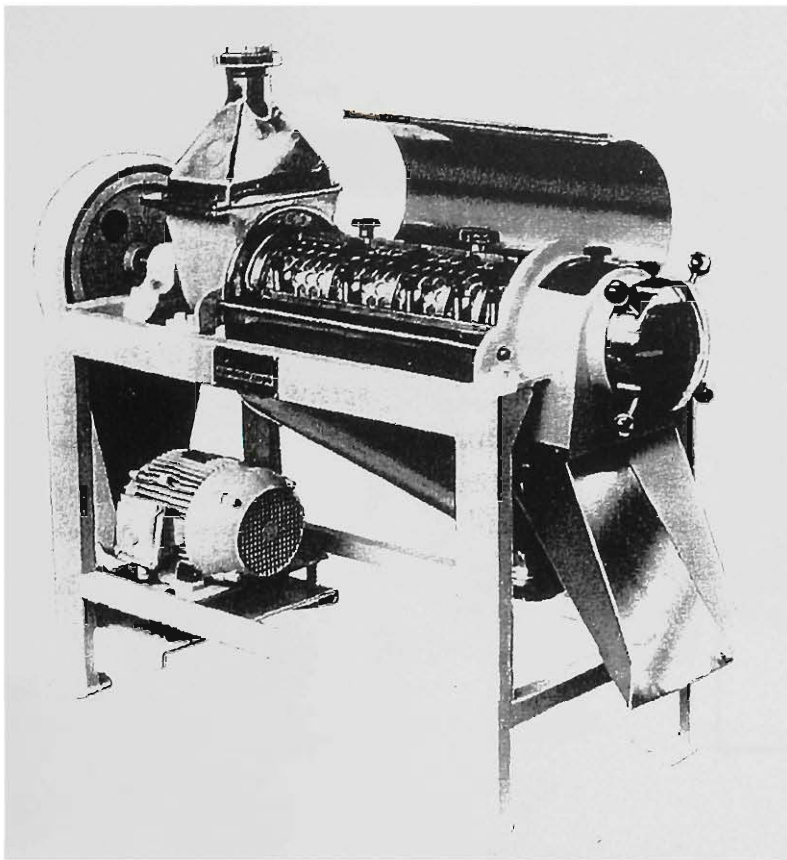


Figure 2.9 Primary screw type tomato juice extractor (Leoni, 1993)

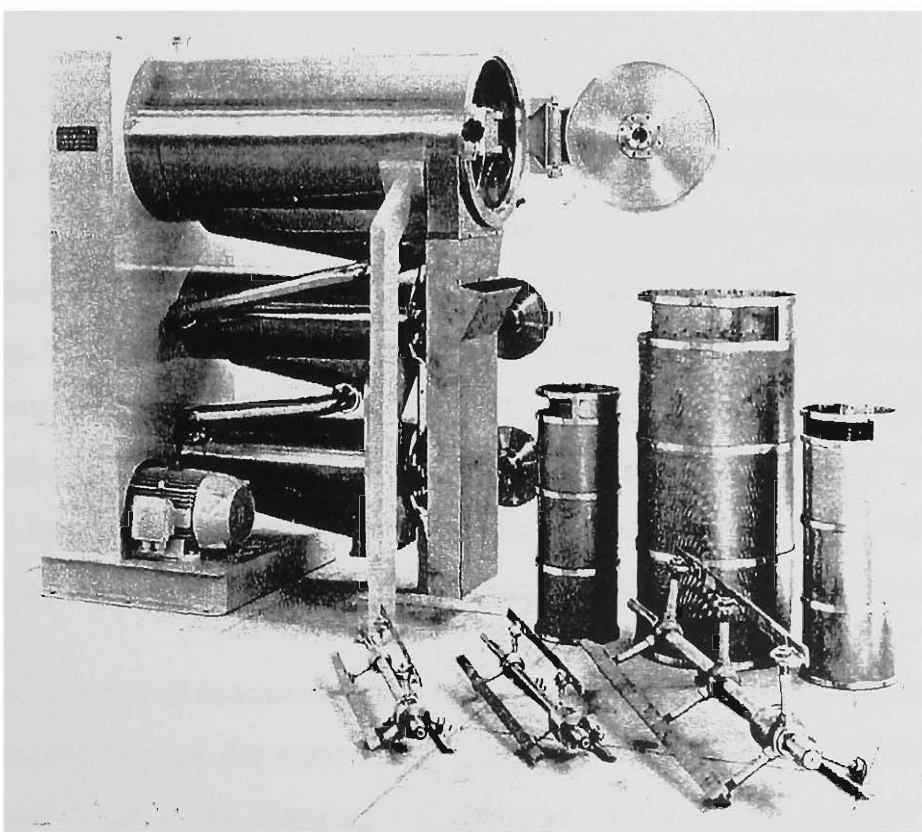


Figure 2.10 Paddle type tomato juice extractor (Leoni, 1993)

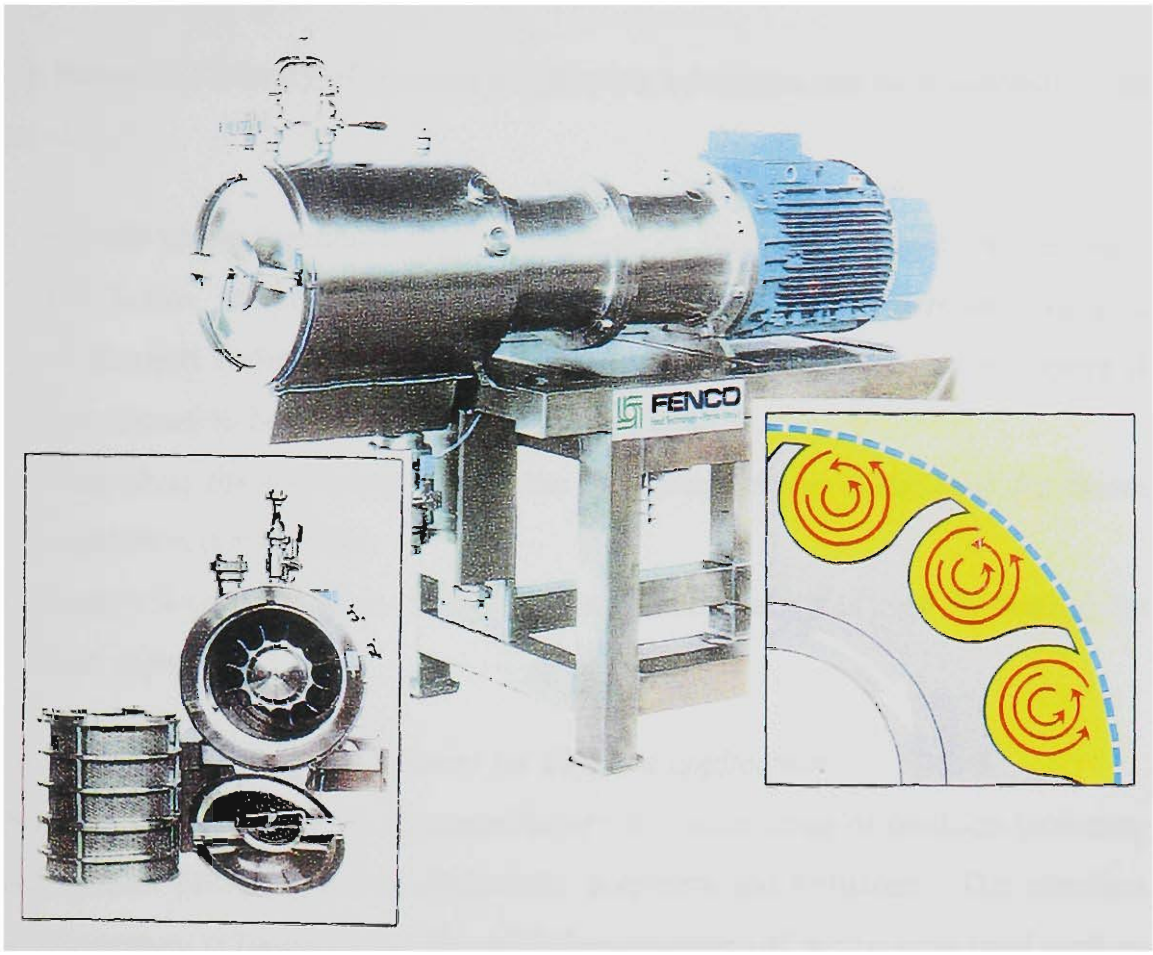


Figure 2.11 Turbo tomato juice extractor (Leoni, 1993)

2.6.1.7. Concentrate preparation by thermal vacuum evaporation

Liquid foods contain water, which limits the shelf-life of the food and make such foods expensive to transport and store. This water is often removed by evaporation or drying. Evaporation involves the partial removal of water unlike drying, which involves the almost complete removal of water. The main reasons for evaporating liquid foods are to: reduce the cost of drying; induce crystallization; reduce costs of storage and transportation; reduce water activity which increases microbiological and chemical stability; recover by-products from waste streams and to induce desired flavour and texture in the final product.

The economics of evaporation is generally influenced by two factors: viz. the loss of concentrate and the energy expenditure (Fellows, 1988). Product losses are generally caused by foaming (protein and carbohydrates tend to reduce heat transfer) and vaporisation (loss of product as mist during boiling).

The thermal efficiency of vacuum evaporation processes can be improved by the use of:

1. Vapour recompression (either mechanical or thermal)- whereby the pressure and hence temperature of vapour from one effect is increased using a mechanical compressor or a steam jet pump and this high-pressure vapour is then reused to heat preceeding effects.
2. Preheating the incoming feed to the evaporator or the water used for steam generation in the boiler.
3. Multi-effect evaporation- where vapour from one effect is used for heating the next effect.

2.6.1.7.1. *Selection of evaporators for different applications*

Evaporation can be used in the manufacture of a wide range of products including food, paper, pharmaceuticals, chemicals, polymers and fertilizers. The selection of evaporators is based on the physical characteristics of the process fluid such as its viscosity, foaming ability, thermal sensitivity, heat transfer coefficient, crystallization ability, freezing point and the recompressibility of the vapour (Mehra, 1986). There are four common types of evaporators used in the food industry, viz. plate evaporators, falling-film evaporators, centrifugal film evaporators and scraped surface film evaporators. The types of evaporators used for food concentration are summarised in Table 2.6.

For the processing of dairy foods, evaporators are generally used for pre-concentration prior to the spray drying process (Murphy *et al.*, 1999). Whole milk and skim milk are first pre-concentrated to approximately 50% total solids by evaporation and then spray dried to moisture content of 3-4%. Improvements in milk evaporation over the years have been well documented (Bouman *et al.*, 1993; Bouman and Waalewijn, 1994). The move from three stage evaporation systems with thermal recompression over one stage to seven stage evaporation with mechanical or thermal recompression over multiple stages has resulted in improvements in economy and product quality (Fluck, 1988; Jebson and Chen,

1997; Yanniotis and Pilavachi, 1994). Many of these advances and improvements have been adapted by other sectors of the food processing industry.

Table 2.6 Common types of evaporators used in the food industry

Application	Evaporator type
Fruit purees	TTF/MVR
Clear fruit juices	FF/TVR
Citrus fruit juices	FF/MC/MVR
Tomato paste	FC/MVR
Milk	FF/MVR/TVR
Liquorice	FF/TTF
Meat extracts	TTF
Fish extracts	FF/TTF

Source: Fenco Food Engineering Co., (1999)

Key: FC - forced circulation MVR - mechanical vapour recompression
FF - falling film TTF - turbulent thin film
MC - mixed circulation TVR - thermal vapour recompression

Modern citrus juice evaporation involves the use of falling film long-tube type evaporators also known as TASTE evaporators (thermally accelerated short-time evaporators), and use high temperatures with very short processing times (Hernandez *et al.*, 1995; Johnson *et al.*, 1996; Teixeira and Shoemaker, 1989). Citrus juice is prone to heat damage and a short residence time is therefore advantageous. On the other hand apple juice is less susceptible to heat damage so is usually processed by any evaporator with a vapour-induced film system (Tonelli *et al.*, 1995).

2.6.1.7.2. *Tomato juice evaporation*

Tomato juice previously used to be concentrated using recirculation evaporators. However, modern tomato evaporators are multi-stage falling film systems with mechanical or thermal compression over at least four stages (Gould, 1996). Due to the use of thermal vapour recompression (TVR) and mechanical vapour recompression (MVR), less steam is consumed and tomato pastes of high total solids content (maximum up to 40 %) can be prepared economically. Evaporators

commonly used for tomato paste production have five stages with three or four effects as well as forced circulation. Forced circulation is accomplished by the use of electrical pumps or steam turbines. The performance data for tomato evaporators manufactured by two major tomato processing equipment companies viz. Fenco Food Engineering Co. and Rossi & Catelli, is summarised in Tables 2.7 and 2.8. Some typical evaporators used for tomato paste production are shown in Figures 2.12 to 2.16.

Table 2.7 Technical data for forced circulation tomato evaporators manufactured by Fenco Food Engineering Co.

Model	Stages and Effects	Evaporated water (kg/h)	Steam Consumption (kg/h)	Water Consumption at 20°C (m^3/h)	Installed Power (kW)	Capacity (t/day) tomatoes ⇒ double concentrate	
F 202	2 effects	3375	1920	49	110	101	16.2
F 205	2 effects	5625	3200	82	130	170	28.44
F 207	3 effects/TVR	7875	4490	114	140	236	37.8
FT 310	3 effects/TVR	11250	4000	102	260	338	54.0
FT 312	3 effects/TVR	13500	4800	122	270	405	64.8
FT 320	3 effects/TVR	22500	8000	204	460	675	108.0
FT 324	3 effects/TVR	27000	9600	245	470	810	129.6
FH 430/H	5 stages/4 effects	33330	9070	265	702	1000	160.1
FH 440/5	5 stages/4 effects	45000	12240	365	700	1350	216.0
FH 470/5	5 stages/4 effects	78750	21420	625	1160	2360	378.0

Source: Fenco Food Engineering Co. (1999)

Table 2.8 Technical data for the Venus tomato evaporators manufactured by Rossi & Catelli

Model	Stages and Effects	Evaporated Water (kg/h)	Steam Consumption (kg/h)	Water Consumption at 20°C (m^3/h)	Installed Power (kW)	Capacity (t/day) tomatoes ⇒ double concentrate	
T 10 DE	2 effect	3500	1800	100	35	104.5	18.2
T 20 DE	2 effect	8000	4100	380	44	240.0	41.6
T 30 DE	2 effect	11000	5600	360	50	331.2	57.2
T 30 TE	3 effect	11000	3750	250	78	331.2	57.2
T 45 TE	3 effect	16500	5700	375	98	496.8	87.5
T 60 TE	3 effect	21000	7150	500	105	633.6	109.2
T 90 TE	3 effect	33000	11200	750	110	993.6	171.6
T 120 TE	3 effect	44000	14800	1000	118	1324.8	228.8
T 120 QE	4 effect	44000	11300	800	260	1324.8	228.8
T 150 QE	4 effect	55000	14000	1000	270	1656.0	286.0
T180 QE/5S	5 stage/4 effect	66000	16900	1200	280	1987.2	343.2
T200 QE/ 5S	5 stage/4 effect	70000	18000	1350	295	2112.0	364.0

Leoni (1993)

Figure 2.12 Two, five stage four effect evaporators (Courtesy, Fenco Food Engineering Co.)

Figure 2.13 Five stage evaporator with mechanical vapour recompression (Courtesy, Fenco Food Engineering Co.)

Figure 2.14 Seven stage evaporator with mechanical vapour recompression (Courtesy, Fenco Food Engineering Co.)

Figure 2.15 Five stage evaporator with steam turbine (Courtesy, Fenco Food Engineering Co.)

Figure 2.16 **Venus triple effect evaporator manufactured by Rossi & Catelli (Leoni, 1993)**

2.6.1.7.3. *Energy consumption during evaporation*

Production of juice concentrates by thermal evaporation is an energy intense process (Yanniotis and Pilavanchi, 1994) and the energy requirements for different evaporators have been reviewed by many researchers (Jebson and Chen, 1997; Ramateke *et al.*, 1993; Rumsey *et al.*, 1984). The performance of evaporators has often been compared to other low temperature concentration methods such as membrane processing and Table 2.9 shows a comparison of the performance of various evaporators with reverse osmosis (RO) for the preconcentration of milk. The RO process requires much less energy for concentration of milk than all of the evaporator types investigated. The most efficient evaporator in this study was the single effect evaporator with mechanical vapour recompression (MVR) which consumed only 65% of the energy consumed by the double effect system, but still consumed 20 times more energy than concentration by RO.

Table 2.9 Comparison of energy consumption and surface areas for preconcentration of milk to 31% TS by evaporators and reverse osmosis

Process	Surface area (m^2)	Energy Consumption (kJ/kg milk)
Open-pan boiling	10.4	1902.9
Double effect evaporator	25.0	874.5
Single effect MVR evaporator	32.0	568.2
RO, batch, single pump	64.5	334.3
RO, batch, dual pump	64.5	28.0
RO, continuous, one stage	206.0	67.8
RO, continuous, three stage	93.0	30.5

Source: Adapted from Cheryan *et al.* (1987)

2.6.1.7.4. *Cost of evaporation*

The economics of the thermal evaporation process is often compared to other less energy-intensive concentration methods such as freeze concentration and reverse osmosis. The basis for cost analysis includes factors such as capital costs, labour,

fuel (gas), steam, cooling water and electricity costs. The data shown in Table 2.10 compares the cost of thermal evaporation (two and four effect systems) with freeze concentration and reverse osmosis. The four-effect evaporator is the least expensive for concentration of liquid foods, followed by the double effect evaporator, freeze concentration and reverse osmosis. This is mainly due to the high fixed cost or the initial capital expenditure associated with the installation of freeze concentration and reverse osmosis systems. The cost of utilities such as power, steam and water is lowest for concentration by reverse osmosis. Significant cost saving was also made by increasing the number of effects. For this reason most evaporators used in the tomato industry for paste manufacture usually have at least four effects (Anon, 1994; Morris, 1991).

Table 2.10 Cost ($ per 1000kg of water removal) of thermal evaporation, freeze concentration and reverse osmosis

Concentration system	Fixed Cost	Utilities	Labour	Total
2 - effect with aroma recovery	0.73	1.29	1.00	3.02
4 - effect with aroma recovery	0.50	0.94	0.42	1.86
Freeze concentration	2.47	1.19	1.68	5.34
Reverse osmosis	5.50	0.1	1.80	7.40

Data adapted from Bomben *et al.* (1993)
Fixed - cost of the initial capital expenditure
Utilities - includes the cost of power, steam and cooling water
Labour - cost of person operating the plant

2.6.1.7.5. *Aroma recovery during evaporation*

The demand for tomato products of improved sensory qualities such as colour and flavour has lead to the investigation of alternative methods of concentration of tomato juice (Porretta, 1993; Porretta *et al.*, 1992; Yildiz *et al.*, 1993). The primary sensory concern during tomato paste manufacture is the loss of volatile components, which are usually associated with the aroma content of the tomato juice. During tomato paste manufacture, longer product residence times in the evaporator can exacerbate the loss of volatile aroma components. Table 2.11 shows typical product residence times in different evaporators used in the fruit

juice industry. The centrifugal evaporator appears to have the shortest residence time and is also able to concentrate products to a higher viscosity than most of the other evaporator types. However it is not widely used in tomato juice concentration and falling film evaporators remain the method of choice.

The aroma recovery process as shown in Figure 2.17 has been used successfully during clarification and concentration of apple and citrus juices (Chen *et al.*, 1991; Sancho and Rao, 1991). Although the aroma recovery process is beneficial for preserving delicate aroma components of fruit juices, often the economics of the process precludes the use of such a step in mainstream food processing. This may be due to the larger volume of steam (expressed as steam equivalents) required for operation of the aroma recovery process (Bomben *et al.*, 1993)

Table 2.11 Typical product residence times and viscosity limits in different types of evaporators

Evaporator type	Stages/passes	Viscosity Limits (mPa.s)	Residence Time
Vacuum pan	1/1	-	> 1 hr
Tubular (rising)	recirculation	100	0.5 - 1 hr
Tubular (rising)	1/1	100	1 min
Tubular (falling)	1/1	200	1 min
Tubular (falling)	5/1	200	4 min
Plate	3/1	300 - 400	4 min
Agitated film	1	20,000	20 - 30 sec
Centrifugal	1	40,000	1 - 10 sec

Ramateke *et al.* (1993)

The aroma of tomato paste can be preserved by:

1. Separation of the aroma components before processing and their re-addition after thermal processing.

2. Processing the juice under conditions that accommodate the retention of aroma components.

3. The addition of artificial or nature identical aromatic compounds after processing.

4. Enzymic regeneration of flavour components in the final product.

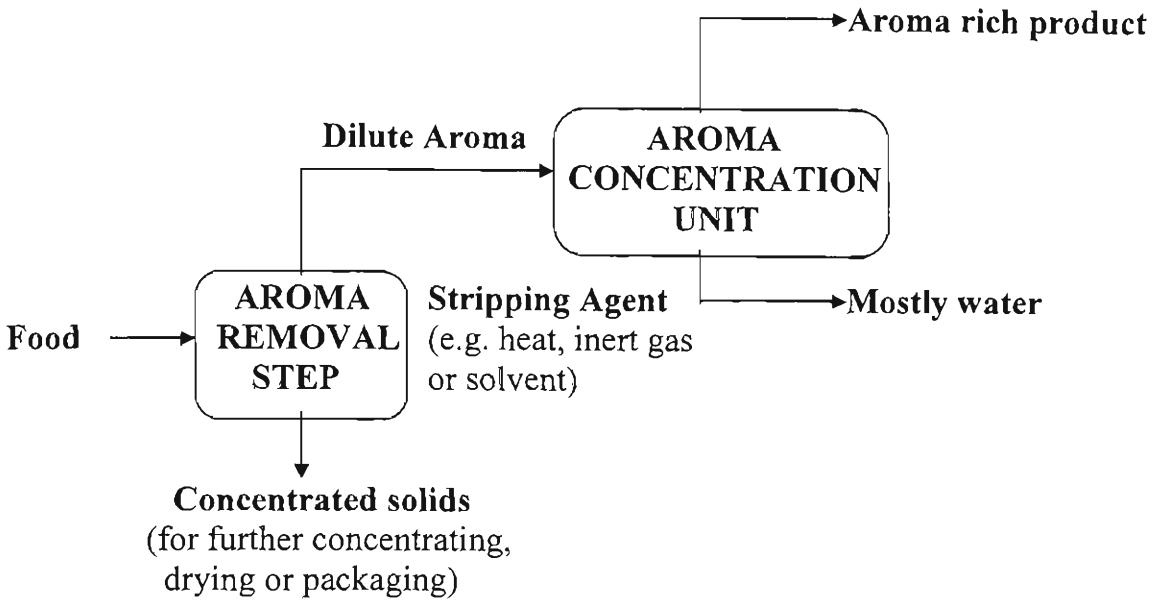


Figure 2.17 General aroma recovery process (Bomben *et al.*, 1993)

2.6.1.7.6. *Effect of evaporators on product quality*

The primary concern during evaporation is the damage to heat sensitive food components such as flavour and aroma compounds. Aroma recovery processes are expensive and their use can significantly affect the cost of the final product. Extended processing times at high temperatures can also lead to formation of an undesirable brown discoloration caused by a compound called 5-hydroxy-methyl-2-furfuraldehyde (HMF) (Porretta and Sandei, 1990; Porretta, 1991). This compound is formed during the reaction between reducing sugars and amino acids in an acidic medium (Mijares *et al.*, 1986). The formation of HMF is directly related to the degree of heating (Toribio and Lozano, 1987). This observation was also noted by Tonelli *et al.* (1995) during the concentration of apple juice where an increase in the HMF content occurred at higher concentration levels of between 30 and 69° Brix and at temperatures of 100°C, 104°C and 108°C. Consequently alternative concentration methods such as reverse osmosis, ultrafiltration and freeze concentration are being used for heat sensitive products that were previously concentrated by vacuum evaporation processes. For example during tomato juice concentration, formation of HMF was reduced by the use of the

ultrafiltration process instead of thermal vacuum evaporation and the use of cold break processes for enzyme inactivation (Porretta *et al.*, 1992).

2.6.1.8. Concentrate preparation by membrane processes

Initially the concept of membrane filtration was used by Samuel Yuster in 1958 for desalination of seawater (Cheryan, 1986). Membrane technology was later extended to removal of microorganisms and particles from fluid and gaseous medium. During the early stages, membrane materials limited the application of membrane filtration. As new materials were discovered the scope of the technology improved and more types of filtration processes were developed. It wasn't until 1963, after the development of reliable organic membranes by Loeb and Sourirajan, that membrane technology became a successful commercial technology (Nielsen, 1992). This new asymmetric membrane was made from cellulose acetate and had salt rejection and flux rates never previously achieved. The removal of salt from seawater achieved by this membrane was based on the application of pressures higher than the osmotic pressure of the seawater. The differential pressure was the driving force for passage of fluid (mainly water) through the membrane. This successful unit operation was initially called hyperfiltration (HF) and it is known today as reverse osmosis (RO).

After its success in desalination operations, membrane filtration subsequently found applications in many areas. Introduction of membrane processes in the food industry commenced with the use of reverse osmosis for the concentration of fruit juices. In 1968, Merson and Morgan investigated the use of membranes for the concentration of orange and apple juices. The resulting flux rates were too low for commercial use and further investigation was necessary to improve the viability of membranes for large scale food processing. With the development of new membrane materials, there was a dramatic improvement in membrane technology and by the early eighties the use of membrane processes for liquid food concentration became an attractive proposition.

2.6.1.8.1. *Types of membrane processes*

Membrane processes involve the selective separation of components in a fluid or gaseous stream across a semi-permeable barrier. Membrane separation is a physical process and involves the retention of larger molecules in a solution called the retentate (concentrate) and the passage of smaller molecules through the membrane in a solution called the permeate. The dynamic flow of liquid through a membrane is shown diagramatically in Figure 2.18. The driving force for the separation is in most cases achieved by pressure, either applied or osmotically induced, except in the case of electrodialysis where separation is influenced by an electrical field (Porter, 1990).

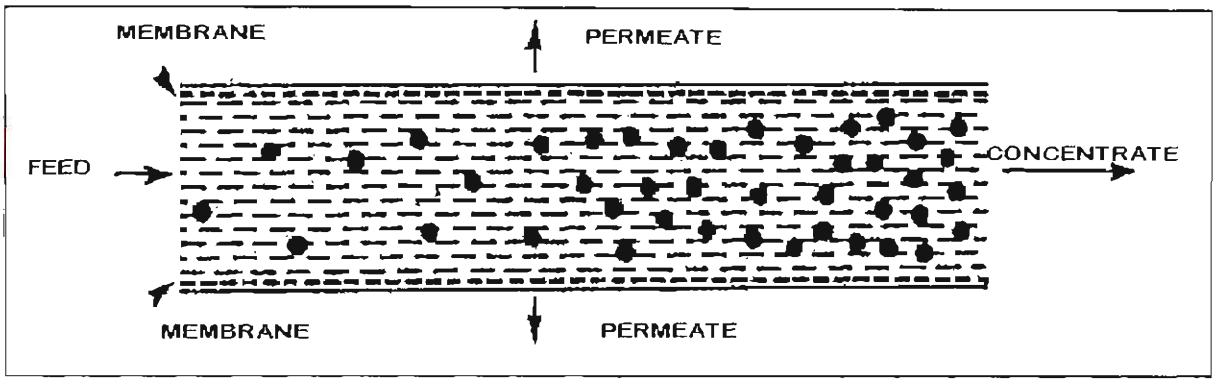


Figure 2.18 Dynamic flow of liquid through a membrane (Glover, 1985)

Membrane processes can be divided into two categories based on the mechanisms of transport. Hydrophilic processes such as ultrafiltration (UF), reverse osmosis (RO) and microfiltration (MF) involve the transport of liquid molecules across the surface of the membrane. On the other hand hydrophobic processes such as membrane distillation (MD) and osmotic distillation (OD) exhibit a different mode of transport and only water vapour is transported across the membrane surface.

Processes such as UF, MF and RO are based on molecular separation. RO effectively retains all molecules except water unlike UF and MF, which retain all particles larger than 10-200 Angstroms (0.001-0.02 μm) (Cheryan, 1986). The distinction between the membrane processes is based on pore size or the molecular weight cut-off (MWCO) of the membrane. Figure 2.19 shows the

various membrane filtration processes and the molecular size of particles separated. Based on particulate separation, reverse osmosis can be used for concentration and desalination processes, ultrafiltration can be used for fractionation, concentration and purification while microfiltration can be used for fractionation, clarification and sterilisation. The types of molecules retained by the various membrane processes are illustrated diagrammatically in Figure 2.20.

The operating conditions such as temperature and pressure used in membrane processes are also distinguishing features that allow some applications to be more successful than others. The type of transport and the chemical structure of the membrane are also unique features of a particular type of separation process and Table 2.12 lists the features that distinguish the three most common membrane processes.

Table 2.12 Comparison of UF, MF and RO processes

Property	**Reverse osmosis**	**Ultrafiltration**	**Microfiltration**
Size of solute retained	MWCO < 500	MWCO < 1000	MWCO >100,000 suspended solids, oils, bacteria, yeast and molds
Osmotic pressure of feed solution	Important, can be over 7000 kPa	Unimportant	Unimportant
Operating pressure	700-15000 kPa	40-700 kPa	15-150 kPa
Nature of membrane	Diffusive transport molecular screening	Screen filtration	Screen filtration depth filtration
Chemical nature of membrane	Important in retention properties	Generally not important	Generally not important
Nature of fouling	Surface fouling	Surface fouling, internal fouling	Internal fouling

Adapted from Luss (1984)

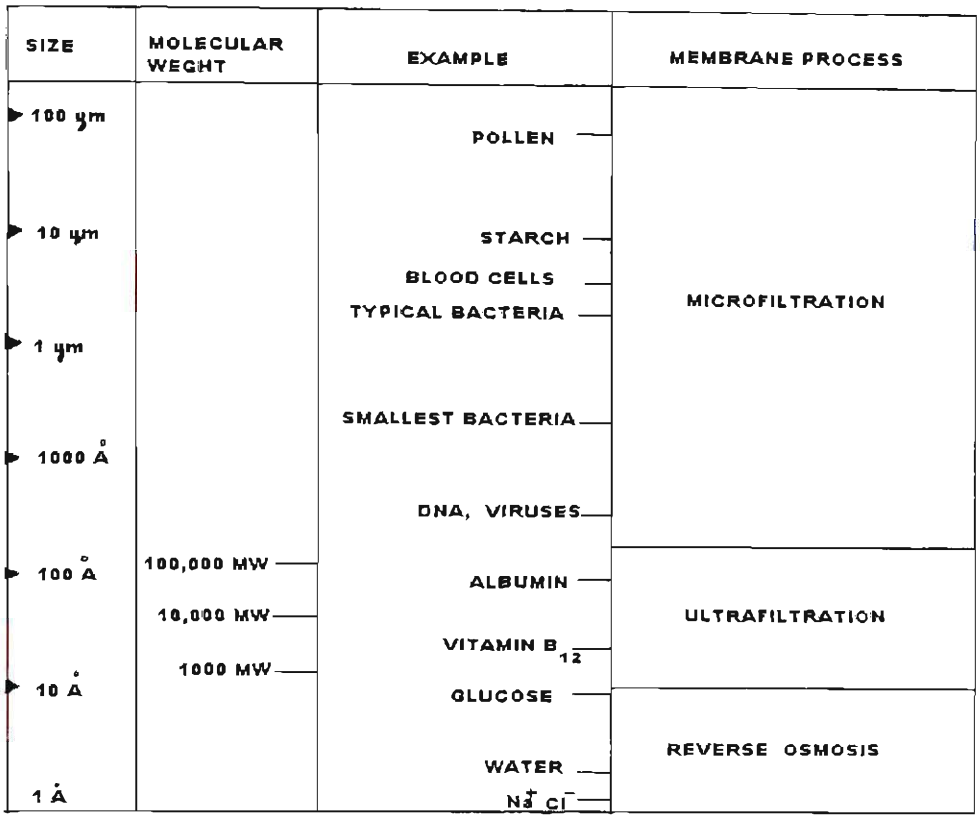


Figure 2.19 Typical components separated by MF, UF and RO membranes (Cheryan, 1986)

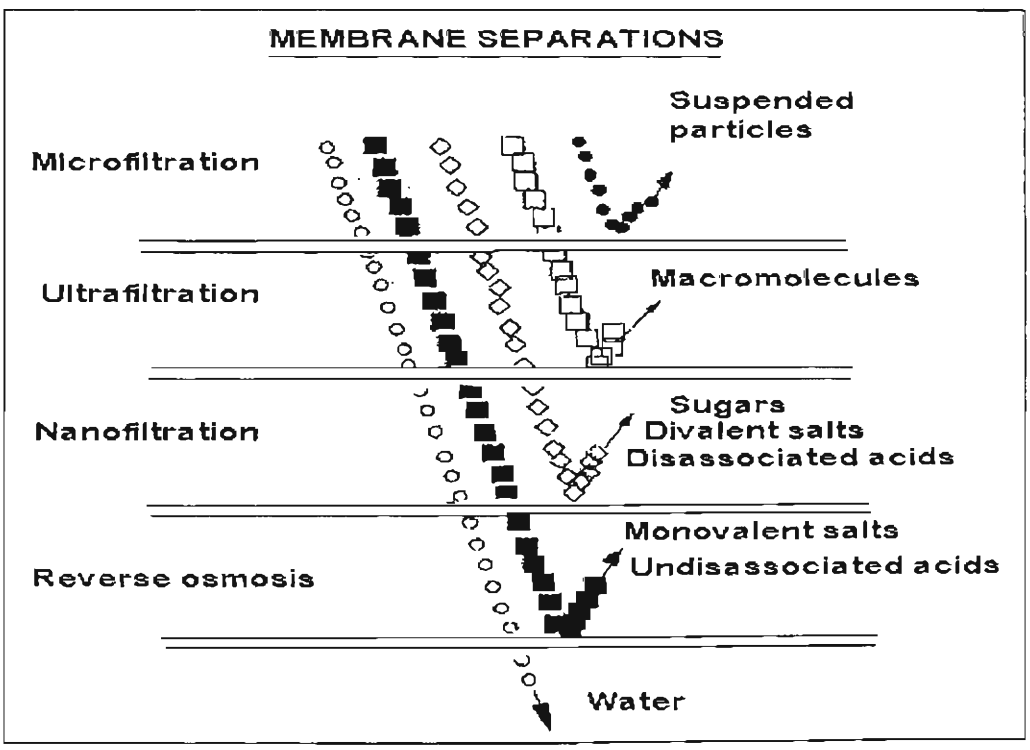


Figure 2.20 The separation characteristics of different membrane processes (Cheryan, 1991)

(i) Microfiltration (MF) process

Microfiltration is a purification process often used to remove suspended particles and microorganisms from feed solutions. Usually a tubular membrane design (see Section 2.6.1.8.2) is more effective for MF processing, however sometimes hollow fiber membranes are used where a low budget installation is required. MF permeate is usually the required product stream and it may contain water, salts, sugars, proteins, enzymes etc. (Marshall, 1990). MF processing is commonly used for clarification of fruit juices and wine (Girard and Fukamoto, 2000; Tragardh, 1995), for recovering whey proteins from whey (Bacher and Konigsfeldt, 2000) and for the reduction of microbial load in liquid milk products (Pedersen, 1991).

(ii) Ultrafiltration (UF) process

Ultrafiltration is usually categorized as a fractionation or concentration process and is largely used for the filtration of macromolecules with MWCO between 500 and 1000 (Mohr *et al.*, 1989). A pressure drop effects the UF process across the membrane surface which in turn selectively allows some particles to pass through and others to be retained. Commercially the UF process can be used for standardisation of milkfat for cheesemaking (Hickey *et al.*, 1990), enzyme manufacture (Jelen, 1991) and for the fractionation of whey during whey concentrate preparation (De Boer and Koenraads, 1991). The UF process has also been used for the clarification of fruit juices such as apple juice (Alvarez *et al.*, 1998; Cliff *et al.*, 2000; Constenla and Lozano, 1995; Fukumoto *et al.*, 1998; Riedl *et al.*, 1998; Su and Wiley, 1998) as well as for concentration of other juices such as pear, orange, pineapple and tomato (Capannelli *et al.*, 1994; Carvalho *et al.*, 2000; Hernandez *et al.*, 1995; Johnson *et al.*, 1996; Vivekanand *et al.*, 2001). Extraction of enzymes and bitter compounds from fruit juices has also be successfully achieved by UF processing (Hernandez *et al.*, 1992; Snir *et al.*, 1996). UF plants can be installed in any of four configurations: viz. plate and frame, spirally wound, hollow fibre or tubular and the choice is largely dependent on the application and budget.

(iii) Reverse osmosis (RO) process

The application of reverse osmosis is mainly for the purification of water, however RO is also very versatile in terms of dewatering and preconcentration of liquid food products. The advantage of the RO process is that only water is removed and this good quality water can be used for other factory processes. High pressures in the order of 15000 kPa are required to overcome the existing osmotic pressure and achieve filtration. The RO process has a wide range of applications such as purification of water, concentration of milk, cheese whey and antibiotics (Pepper, 1990). The RO process has also been successfully used for the concentration of fruit juices such as apple (Chou *et al.*, 1991; Kumar *et al.*, 1992) lemon (Kane *et al.*, 1995) mango (Olle *et al.*, 1997), orange (Koseoglu *et al.*, 1990; Walker, 1990), tomato (Pepper *et al.*, 1985; Yildiz *et al.*, 1993) and watermelon (Suh *et al.*, 2001). Unlike MF and UF processes, RO is limited to particulate-free feed streams and can only achieve relatively low concentration levels of up to 20% total solids level due to the diminishing flux rate.

(iv) Isothermal membrane distillation (IMD) process

The IMD process is a patented membrane system specifically developed for the concentration of heat sensitive food, beverage and pharmaceutical products (Lefebvre, 1986). Concentration is facilitated by the means of an osmotically induced vapour pressure gradient across a hydrophobic membrane as shown in Figure 2.21. The use of low temperature during processing enables the preservation of desirable sensory qualities such as colour, flavour and aroma. Pilot trials have shown that IMD/OD is a suitable process for concentrating wine (Thompson, 1991; Wilson and Peterson, 1992;) as well as fruit and vegetable juices (Johnson *et al.*, 1989; Kunz *et al.*, 1996; Mengual *et al.*, 1993; Petrotos and Lazarides, 2001; Skurry and Nugyen, 1992). IMD/OD can also be used to separate food components such as removal of alcohol from wine (Mermelstein, 2000). A typical OD/IMD system is shown diagrammatically in Figure 2.22.

Concentration by IMD involves two major unit operations in which a product or feed stream and a brine solution are passed over the two surfaces of a hydrophobic membrane. The concentrated brine solution, usually between 50 and 70 °Baume,

draws water from the feed stream in effect diluting itself. This brine solution, often called a brine stripper can be made from calcium, potassium or sodium salts. Potassium salt solutions are more commonly used because they are less corrosive than other salts and also due to their higher water solubility (Hogan *et al*, 1998). The IMD process is described (Johnson and Bailey, 1994) as a mass transport process and can be summarized by the following three steps:

Stage 1: Evaporation - water lost to evaporation at feed-membrane interface.

Stage 2: Diffusion - water vapour diffuses from the liquid product through membrane pores.

Stage 3: Adsorption - diffused water adsorbed by the brine stripper

Currently IMD is only suitable for clarified feed streams and is limited in its use by the availability of suitable membrane materials. Good membrane performance during IMD processing can be achieved by pretreatment of feed by ultrafiltration and by careful selection of membrane type. Membrane configuration also contributes to the efficiency of product flow and the final concentration level achieved.

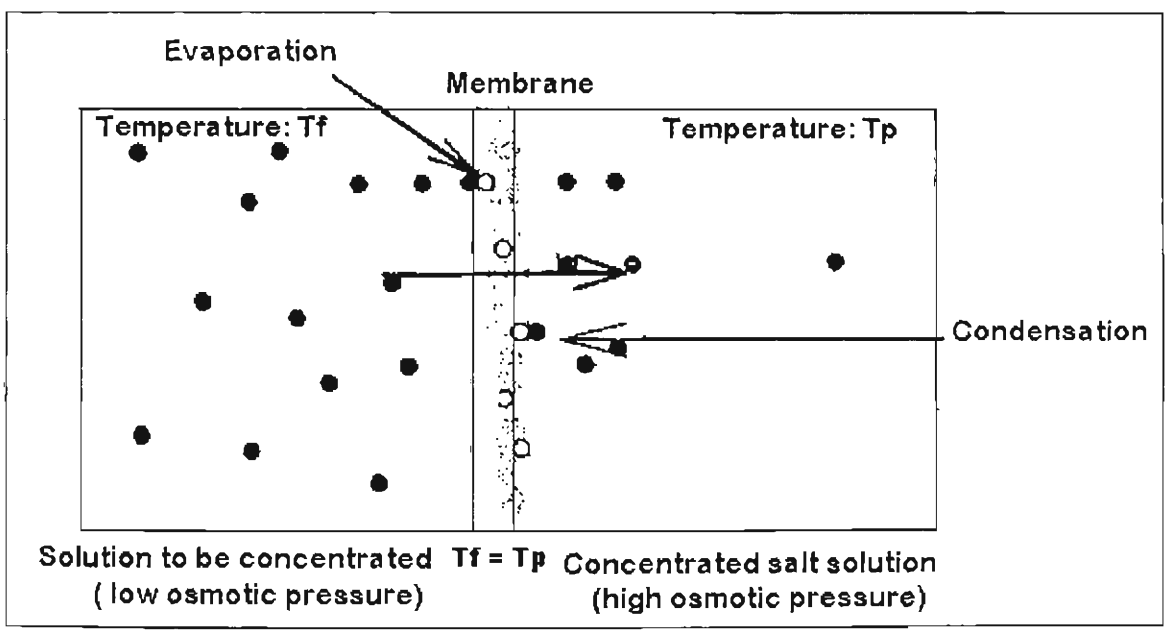


Figure 2.21 **Osmotic evaporation effected by a pressure gradient (Kunz *et al.*, 1996)**

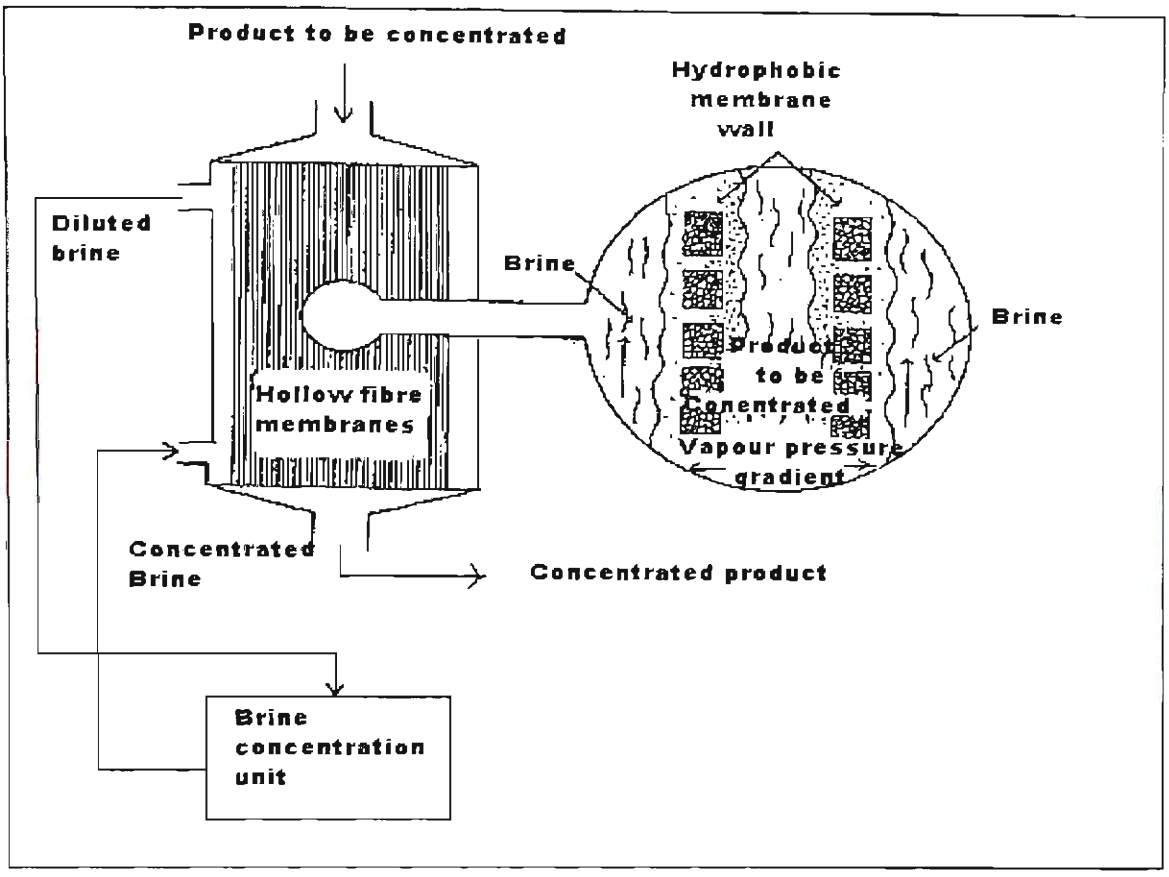


Figure 2.22 Isothermal membrane distillation (IMD) unit (Johnson *et al.*, 1989)

2.6.1.8.2. *Membrane configurations*

Filtration modules used for membrane separation processes are available in four different configurations, viz. tubular, plate and frame, hollow fibre, and spiral wound. Some of the configurations are limited in their applications due to membrane performance and the physical properties of the feed solutions. The following list shows the suitability of the different designs for particular membrane processes:

Membrane Configuration	Typical Process Applications
Spiral-wound	UF, RO and IMD
Plate and frame	UF, RO and IMD
Tubular	MF, UF, RO and IMD
Hollow fibre	MF and UF

Adapted from Teknotext AB (1995)

(i) Tubular module

In the tubular modules, the membrane is cast on to a glass or paper tube that is inserted into a perforated stainless steel support tube. These tubes are bundled together in a stainless steel shell as shown in Figure 2.23. The internal tube diameter ranges between 12 and 25 mm and the lengths are usually between 0.6 and 6.4 m (Macrae *et al.*, 1993). This type of module is capable of handling feed streams with both a high viscosity and a high-suspended solids level (Cheryan, 1986).

(ii) Plate and frame module

In this configuration flat sheets of membrane are placed between support plates. These plates are horizontally sandwiched and stacked together in such a way that the flow channels are formed between the plates. Feed is pumped between these plates as shown in Figure 2.24 (Macrae *et al.*, 1993). This membrane design is not capable of handling viscous feeds and can be difficult to clean.

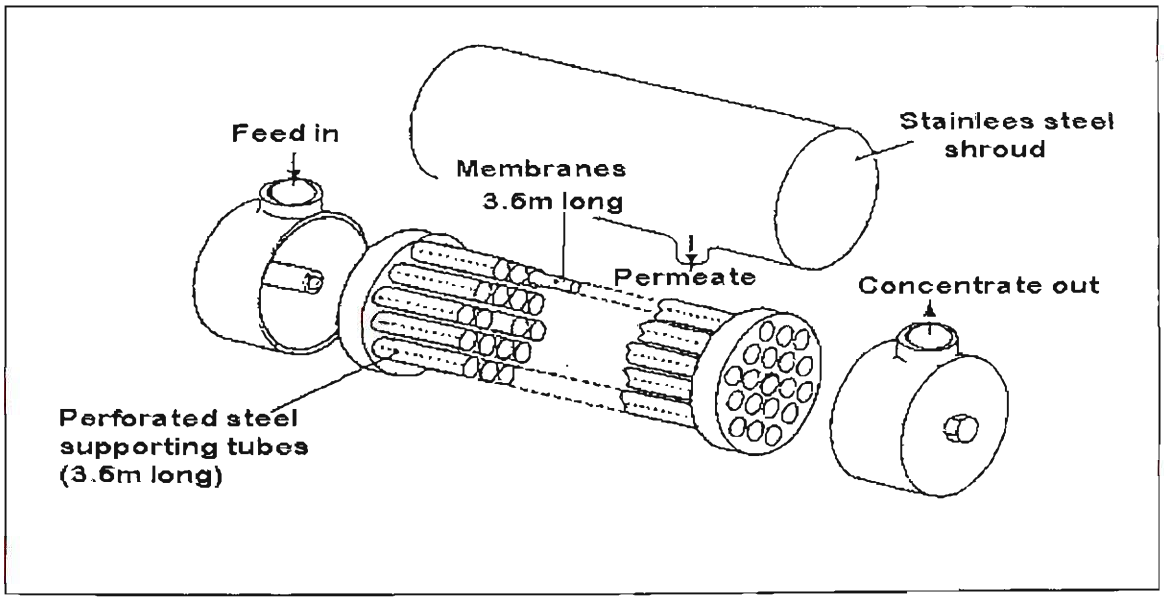


Figure 2.23 Tubular membrane configuration (Glover, 1985)

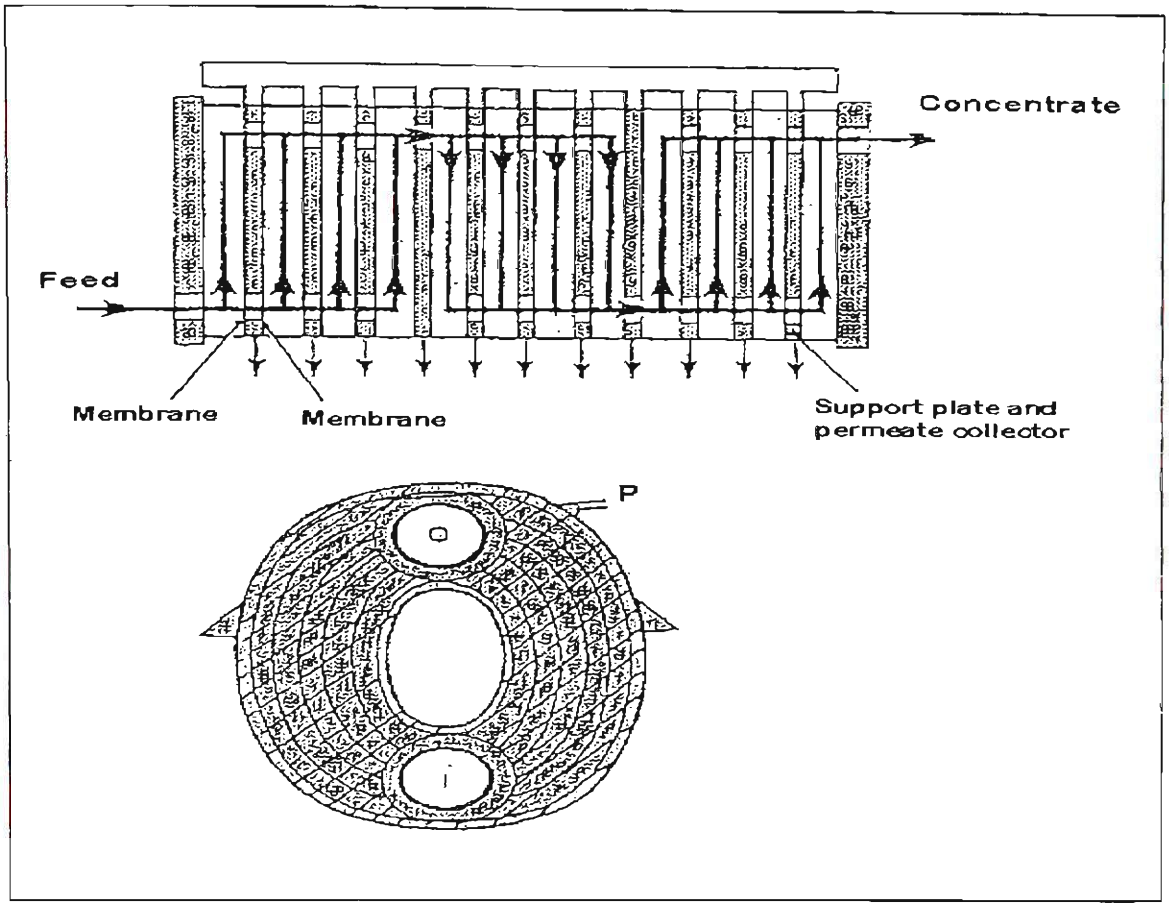


Figure 2.24 Plate and frame configuration (Glover, 1985)

(iii) Hollow fibre module

This configuration involves the formation of membranes on the inside of self-supporting tubes that have an internal diameter in the range of 1 mm (Macrae *et al.*, 1993). Hundreds of these tubes are inserted and glued in a cartridge to form a shell and tube arrangement as illustrated in Figure 2.25. Lack of proper membrane support limits operating pressures and this design is only suitable for low viscosity feed streams (Cheryan, 1986).

(iv) Spiral wound module

This module is similar to the plate and frame, except there are two flat sheet membranes with a mesh spacer between them. The membrane is attached along three sides and the fourth side is pasted to a perforated tube which forms the permeate channel. A mesh spacer envelopes this whole arrangement which is wound around a central permeate collection tube (Macrae *et al.*, 1993) as shown in Figure 2.26. This membrane design is also unsuitable for viscous feeds.

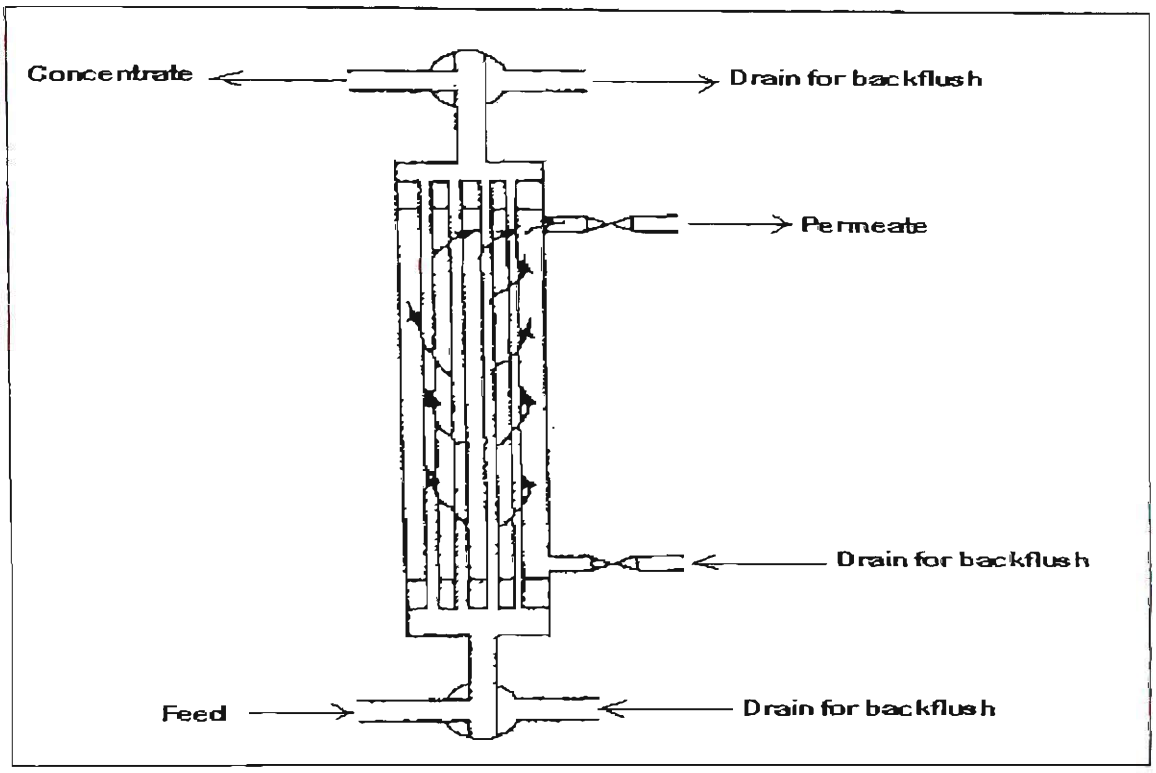


Figure 2.25 Hollow fibre configuration (Glover, 1985)

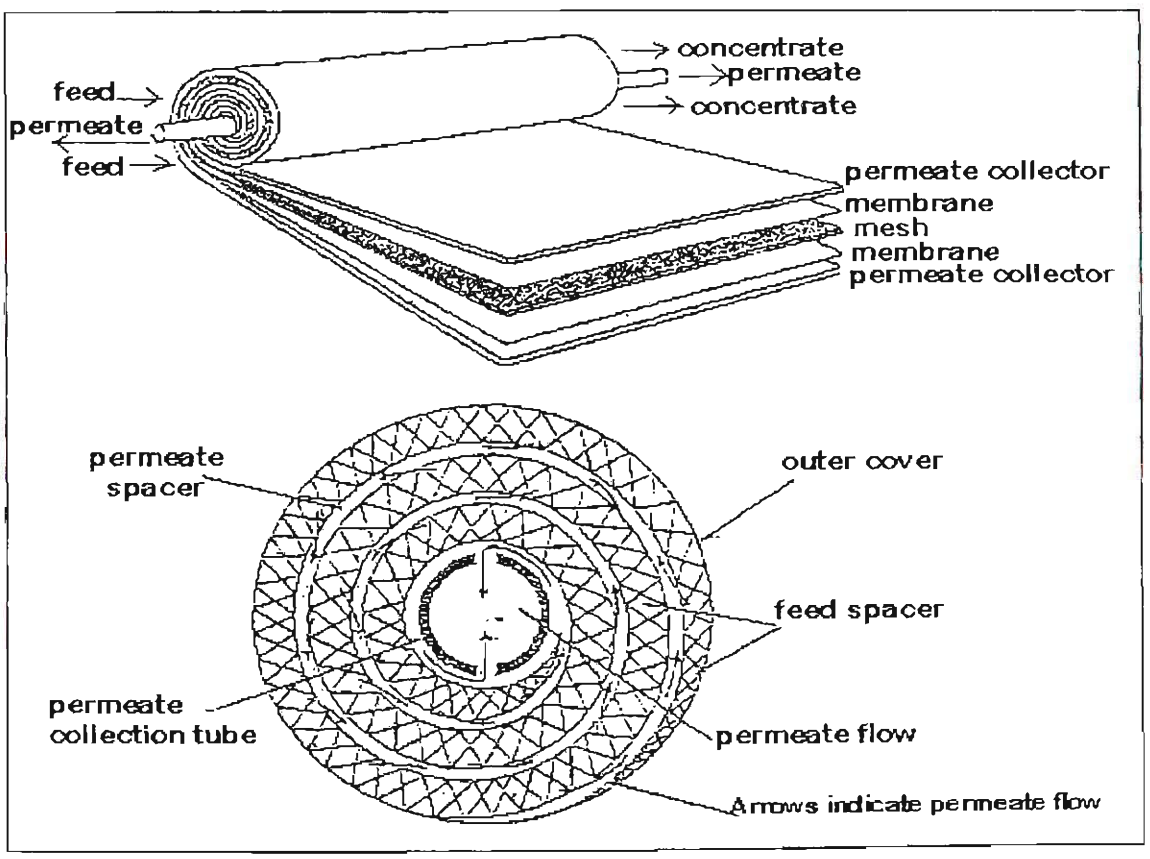


Figure 2.26 Spiral-wound configuration (Glover, 1985)

2.6.1.8.3. *Performance of different membrane configurations*

Module designs are usually chosen based on the physical properties of the feed stream and other factors such as flux rate, ease of soil removal, sensitivity to fouling, resistance to pH extremes and durability during cleaning. The advantages and disadvantages of the four common module designs are summarized in Table 2.13.

Table 2.13 Advantages and disadvantages of membrane module designs

Module Design	Advantages	Disadvantages
Tubular	• Can process feeds with large suspended particles. • Easy to clean by CIP. • Individual membranes can be replaced on site.	• Need efficient pumping. • High pressure drop. • High energy consumption. • Low surface area to volume ratio. • High floor space required to install plant. • High hold up volume.
Plate and frame	• Economic in energy terms. • No special pumps needed • Good with viscous solutions. • Can attain high concentration. • Low retention volume. • Minimum floor space required. • Membrane replacement easy.	• Difficult to clean. • Susceptible to plugging.
Hollow fibre	• High surface area per unit volume. • Low retention volume. • Improved cleanability by back flushing. • Low energy consumption.	• Fibres are susceptible to plugging at the cartridge inlet. • Low pressure limits use. • Difficult to maintain high flow with high viscous solutions in long cartridges.
Spiral wound	• High surface area per unit volume. • Minimum floor space required. • Low capital and operational costs. • Low retention volume.	• High pressure drop-unsuitable for viscous solutions. • Difficult for solutions with high suspended solids. • Mesh spacer creates dead spots - retains particles. • Difficult to clean. • Difficult to replace membrane - need to change whole module.

Source: Renner and Abd El-Salam (1991)

2.6.1.8.4. Membrane materials

Membrane filtration technology has advanced rapidly due to the discovery of many new materials and processes by which membranes can be manufactured. Cheryan (1994) suggested that over 130 materials are suitable for membrane

processing but only a few are approved for food use by the United States Food and Drug Administration (FDA). The first generation membranes consisted of polymeric and integrally skinned membranes. The second-generation membranes were manufactured as thin film composites. The third and present generation membranes are non-polymeric and made of mineral/ceramic materials (Cheryan, 1994). Membrane types, materials and methods of manufacture together with processes in which they are used are summarised in Table 2.14.

Table 2.14 Membrane type, material and method of manufacture

Type	Membrane Process and Membrane Type	Formation Procedures	Membrane materials
Polymeric	Reverse osmosis Integrally skinned Thin film composite	Phase inversion Interfacial polymerization	Cellulose acetate, polyamide, polyamide/polysulphone
	Nanofiltration Thin film composite	Similar to RO	Similar to RO but actively charged
	Ultrafiltration Integrally skinned Formed-in-place	Phase inversion Dynamic formation	Polysulfone, polyacrylonitrile, polyvinylidene fluoride Alginate salt on TiO_2
	Microfiltration Integrally skinned Formed-in-place	Phase inversion Dynamic formation	Polypropylene, polysulfone, poly ether sulfone, nylons(6, 66), polyvinylidene fluoride, cellulosics Alginate salt on TiO_2 polyvinyl alcohol on TiO_2
Inorganic	Microfiltration Ultrafiltration	Molding and sintering of fine-grain powders	Alumina, Zirconia, stainless steel, carbon composite, silica

Source: Renner and Abd El-Salam (1991)

(i) Polymeric membranes

Polymeric membranes are made from materials such as cellulose acetate, polysulfone, polypropylene, polyvinylidene fluoride, regenerated cellulose, polyamide and polycarbonate. The main advantages of using polymer membranes include the low cost and the variety of separation processes that can be performed.

Cellulose acetate (CA)

The cellulose acetate membranes were the most common types of membranes utilized in early membrane technology studies. The major reasons for the use of

CA membranes were the ease of fabrication, their low cost, the high salt retention and the relatively high flux (Mohr *et al*, 1989). However the use of CA is subject to limitations such as a low temperature tolerance of a maximum of 35°C, a restricted usable pH range between 3 and 7 and a low resistance to cleaning chemicals, in particular chlorine. CA membranes also can undergo "creep" or a compaction phenomenon which causes a gradual decrease in the flux rate (Lonsdale, 1972).

Polysulfone (PS)

Membranes made from aromatic polysulfones such as polyphenylsulfone, polyethersulfone, polyarylsulfone and sulfonated polysulfone are well suited for use in the food industry. PS membranes are resistant to high temperatures of up to 150°C and have a wide usable pH range of 3 to 11. PS membranes also have excellent resistance to cleaning and oxidizing chemicals. The PS membranes are usually prone to fouling, particularly during whey processing (Horton, 1990). Only ultrafiltration and microfiltration membranes are made from PS polymers.

Polyamides (PA)

PA membranes are usually thin film composite membranes that have excellent retention of low molecular weight organic compounds. Usually PA membranes are used in the place of CA membranes due to their better tolerance to high temperatures of up to 80°C and a broader usable pH range of between 3 and 11. PA membranes can be cleaned with acid and caustic detergents but are extremely sensitive to chlorine. Sanitation can be achieved by short-term heat treatment at temperatures around 77°C (Mohr *et al.*, 1989). PA membranes are most commonly used in reverse osmosis processes due to their high retention of solutes.

Polyvinylidene Fluoride (PVDF)

PVDF membranes have been used to replace CA membranes in the dairy industries (Mohr *et al.*, 1989). Usually PVDF as a polymer can withstand harsh chemicals but when cast as a membrane in asymmetric form it has poor tolerance to caustic cleaning agents particularly in the presence of chlorine (Horton, 1990).

Generally PVDF membranes are hydrophobic but are often modified so that they can be used in hydrophilic membrane processes.

Polytetrafluroethylene (PTFE)

PTFE or 'Teflon' membranes are stable to high temperatures in the range 100°C to 260°C and resistant to very strong acids and alkalis (Cheryan, 1986). They are extremely hydrophobic and are mainly available in pore sizes in the MF range. They are usually used for the treatment of vapors and gases.

(ii) Inorganic membranes

Inorganic membranes are usually made from materials such as alumina, zirconia, stainless steel, carbon composite and silica. These membranes are well suited to the food industry because of their tolerance to extreme processing conditions and resistance to harsh cleaning and sanitizing chemicals. The processing advantages of these membranes result from their greater structural strength and resistance to abrasive degradation. The most distinctive feature is the ability of these membranes to withstand very high temperatures of up to 250°C (Mohr *et* al., 1989) in addition to wide pH limits of between 1 and 13. Membrane limitations include the cost, the fragility and the restriction of pore size to mainly microfiltration processing (Cheryan, 1994). The inorganic membranes have a further limitation of design because they are only available in tubular configuration, which reflects in the cost of installing such membranes systems. At present only ultrafiltration and microfiltration processes can be performed with inorganic membranes.

(iii) IMD membranes

Membranes suitable for IMD processing are usually made from hydrophobic microporous materials such as polypropylene, polyvinylidene fluoride (PVDF) or polytetrafluroethylene (PTFE). Table 2.15 shows some of the typical characteristics of microporous hydrophobic IMD membranes. As summarised in Table 2.16, the Sumitomo and Gortex membranes manufactured from PTFE have the highest mass transfer coefficients and are best suited to IMD processing; however the Sumitomo membrane lacked durability during extended hours of

IMD processing (Johnson and Bailey, 1994). Significant membrane resistances were noted for Millipore and Accurel membranes, which reflected in the low mass transfer rates (see Table 2.16) for these membranes.

Table 2.15 Properties of hydrophobic microporous IMD membranes

Membrane type	Polymer	Mean Pore Diameter x 10^6 m	Thickness x 10^6 m	Porosity μm
Celguard 2400	Polypropylene	0.05	25	0.38
Celguard 2500	Polypropylene	0.12	25	0.45
Millipore- VVSP	Surface-modified PVDF	0.1	120	-
Millipore - GVSP	Surface-modified PVDF	0.2	120	-
Accurel - 1E- 2P	Polypropylene	0.1	75 -110	-
Accurel - 2E - 2P	Polypropylene	0.2	130-170	-
Accurel - 2E -HF- 2P	Polypropylene	0.2	140-180	-
Gortex L31189	PTFE	0.2	50	0.6
Sumitomo - 045 - 40	PTFE	0.45	50	-
Sumitomo - 020 - 40	PTFE	0.2	50	-

Source: Johnson and Bailey (1994)

Table 2.16 Membrane resistance, transfer coefficient and flux rate for some common IMD membranes

Membrane type	Membrane Resistance to Mass $\frac{r\varepsilon}{l\chi} \times 10^5$	Mass Transfer Coefficient $k_m \times 10^6$ (ms^{-1})	Flux $kg.m^{-2}.h^{-1}$
Celguard 2400	2.59	0.24	0.51
Celguard 2500	13.4	1.22	2.63
Millipore- VVSP	25.2	2.29	4.94
Millipore - GVSP	59.7	5.43	11.7
Accurel - 1E- 2P	26.1	2.38	5.12
Accurel - 2E - 2P	53.8	4.90	10.6
Accurel - 2E -HF- 2P	81.1	7.37	15.9
Gortex L31189	96.3	8.74	18.9
Sumitomo - 045 - 40	97.1	8.85	19.0
Sumitomo - 020 - 40	131	11.94	25.7

Source: Johnson and Bailey (1994)

2.6.1.9. Quality parameters influenced by thermal processing

Most foods are heat treated to inactivate deteriorative enzymes and destroy microorganisms. Although the shelf stability of the food is improved by thermal treatment, other heat sensitive food components such as vitamins, pigments and aroma compounds can be destroyed or altered during the process. For the purpose of achieving high quality, researchers have continuously investigated technologies that require minimal thermal processing hence retaining some of the sensory properties that define better eating quality (Porretta, 1993; Porretta *et al.*, 1992; Yildiz *et al.*, 1993). During tomato concentrate preparation the three main sensory parameters colour, consistency and flavour are commonly used to assess the quality of final concentrates. Due to the absence of worldwide standardization of methods and instruments to define tomato paste quality, several major tomato

processors have developed internal company standards to characterise uniform quality (Hayes *et al.*, 1998).

2.6.1.9.1. *Colour*

The most important constituent responsible for colour in tomatoes is the carotenoid pigment lycopene (shown in Figure 2.27), which comprises about 83% of the carotenoid content in tomatoes (Thakur *et al.*, 1996). Lycopene, due to the unsaturated carbon chain is susceptible to oxidation, which is accelerated by light, metals and peroxides (Klein, 1992). In addition to oxygen, heat processing also causes a structural change in the lycopene from a trans form to a cis form (Klein *et al.*, 1985). For this reason tomato processors use low temperature processes such as the use of cold break processes for enzyme inactivation and membrane processes for concentration of tomato juice to tomato pastes. To enhance final tomato paste colour, processors also use tomatoes of high lycopene content that have been ripened on the vine to the red-ripe stage.

The colour of processed tomato products is also affected by other factors such as the sugar content, acidity and other brown pigments. The formation of brown pigments during tomato processing is the result of three types of non-enzymatic browning reactions. The first is Malliard browning which occurs as a result of reactions between the reducing sugars and proteins (amino acids) contained in the tomato juice (Daood *et al.*, 1990). The second is the dehydration reaction of heating reducing sugars in an acidic medium to form furfuraldehydes (F) and hydroxymethylfurfuraldehydes (HMF) (Porretta and Sandei, 1990), the structures of which are shown in Figures 2.28 and 2.29 respectively. Since higher processing temperatures accelerate formation of HMF, several studies reported the use of lower enzyme inactivation temperatures (Porretta, 1993). The third type of non-enzymatic browning is due to caramelisation reactions of primary sugars to form aldols and aldehydes, which is often desired to highlight certain flavour notes, but which can also cause burnt, bitter and acrid notes in foods. Although the Malliard and dehydration sugar-protein reactions do not affect the final flavour they can significantly degrade the colour of processed tomato products (Porretta and Sandei, 1990).

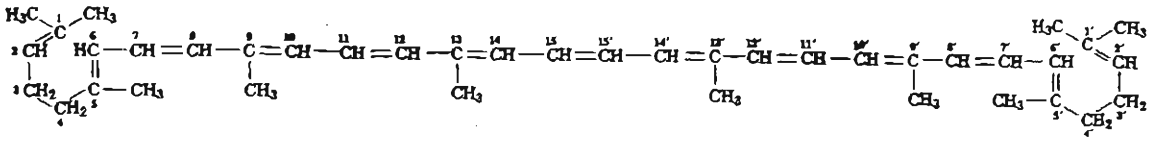


Figure 2.27 Chemical structure of lycopene

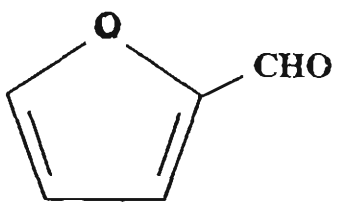


Figure 2.28 Chemical structure of furfural

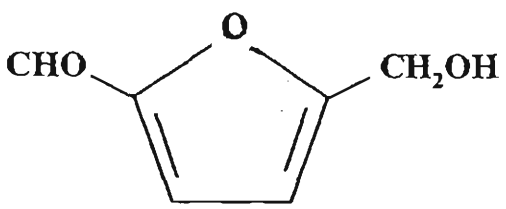


Figure 2.29 Chemical structure of hydoxymethylfurfuraldehyde

2.6.1.9.2. *Consistency*

The consistency of tomato products is dependent entirely on the viscosity of the initial juice, which in turn is dependent on the pectic component of the fresh fruit. In order to maximize the viscosity in the final product, the degree of pectin degradation has to be kept to a minimum. Pectic enzymes such as PME and PG can affect the final viscosity of tomato concentrates and require immediate inactivation (Wong, 1995). The reactions of these pectic enzymes are described in detail in Section 2.6.1.4. The initial thermal break process is carried out at temperatures in excess of 90°C to ensure complete and rapid inactivation of these deteriorative enzymes (Luh and Kean, 1988). The duration and temperature of this initial break process directly affects the consistency and viscosity of tomato pastes (Storforos and Reid, 1992). High break temperatures are advantageous for obtaining good consistency and texture but often compromise other important quality attributes such as colour and flavour (Hayes *et al.*, 1998).

2.6.1.9.3. *Flavour*

The flavour of food components is the most compromised sensory attribute during thermal processing and the volatile flavour component of fresh tomatoes is entirely different to that of the processed tomato products (Buttery *et al.*, 1990b). The flavour of tomatoes is generally affected by climatic and agricultural practices (Davies and Hobson, 1981). Thakur *et al.*, (1996) reported that although tomatoes contain up to 400 different volatile compounds, only a few such as hexanal, trans-2-hexanal, cis-3-hexanal, cis-3-hexanol, trans-2-trans-4-decadienal, 2-isobutylthiazole, 6-methyl-5-hepten-2-one, 1-penten-3-one and β-ionone affect the flavour of fresh tomatoes. It also has been suggested that the hexanal and hexanols are the compounds that suffer the most degradation during thermal processing (Frenkel and Jen, 1989). Some common volatile compounds that change during tomato processing are summarised in Table 2.17. Some researchers have reported that the characteristic flavour associated with processed tomato products is due to the hydrolysis of glycosides (Thakur *et al.*, 1996) and formation of compounds such as dimethylsulphide, β-damascenone, β-ionone, 3-methylbutanal, 1-nitro-2-phenylethane, eugenol, methional, 3-methylbutyric acid,

6-methyl-5-hepten-2-one, phenylacetaldehyde and linalool (Buttery *et al.*, 1990b). Other researchers have studied the odour threshold of components associated with processed tomato paste flavour and have concluded that an addition of 0.7 mg/L of furaneol in a synthetic mixture resembling commercial paste, can significantly improve the taste of tomato paste (Buttery *et al.*, 1995). Although the concentration of most volatile compounds decreases during processing, some products are formed during thermal processing as shown in Table 2.18, and a number of these compounds contribute to the overall flavour of tomato paste (Buttery *et al.*, 1990b).

2.6.1.9.4. *Nutritive value*

Generally during the thermal processing of tomato products, the nutritive value is often overlooked since it does not affect the taste and physical characteristics of concentrates. Tomatoes are a good source of various vitamins and minerals (Redenbaugh *et al.*, 1992), and in particular vitamins A and C (Davis and Hobson, 1981; Thakur *et al.*, 1996). The vitamin content of fresh tomatoes and tomato paste is presented in Table 2.19. It appears that of all the vitamins contained in tomatoes, vitamin C is the most adversely affected by thermal processing. Some researchers have monitored the levels of vitamin C during different stages of processing and concluded that no significant changes in vitamin C levels occurred during the enzyme inactivation stage and only small changes were observed at the concentration stage (Trifiro *et al.*, 1998). However this finding is contrary to that reported by Fonseca and Luh (1976). The major carotenoid lycopene has also recently been found to be effective in preventing certain cancers (Giovannucci *et al.*, 1995; Narisawa *et al.*, 1996; Khachik *et al.*, 1998). Some research also suggests that the lycopene in processed tomato paste is absorbed better than that found in fresh tomatoes (Stahl and Sies, 1992).

Table 2.17 Some volatile compounds in fresh tomatoes and tomato paste

Compound	Fresh Tomato (ppb)	Tomato paste (ppb)
hexanal	3100	4-14
trans-2-hexanal	270	0-5
cis-3-hexanal	12000	0-3
cis-3-hexanol	150	0-15
2-isobutylthiozole	36	3-9
1-penten-3-one	520	0-8
β-ionone	4	0-4
6-methyl-5-hepten-2-one	130	50-1030

Source: Buttery *et al.* (1990b)

Table 2.18 Volatile compounds formed after thermal processing

Compound	Fresh Tomato (ppb)	Tomato Paste (ppb)
dimethyl sulphide	0	800-10000
acetoin	0	100-300
furfural	0	70-210
methaniol	0	1-4
2-acetylfuran	0	18-80
2-pentylfuran	0	3-13
α-terpineol	0	9-54
6-methyl-3,5-hepatadien-2-one	0	2-14

Source: Buttery *et al.* (1990b)

Table 2.19 Vitamin content of fresh tomatoes and tomato paste

Vitamin	Quantity in Fresh Tissue (mg/100g)	Tomato Paste (mg/100g)
A	0.19 - 1.67	0.00
B_1	0.02 - 0.08	0.12
B_2	0.02 - 0.08	0.08
B_3	0.28 - 0.34	2.80
B_6	0.050- 0.15	-
B_{12}	0.30 - 0.85	-
C	8.40 - 59.0	15.0

Source: Redenbaugh *et al.* (1992); English and Lewis, (1992)

2.7. Review summary

Tomatoes are grown in Australia for fresh consumption as well as for processing. The composition of tomatoes and tomato products is affected by factors such as variety, stage of maturity, climatic conditions, disease and seasonal variation. If tomatoes are consumed raw in large quantities they become a valuable source of vitamins A and C. Tomatoes also have a high lycopene content and recent research suggests that lycopene is a useful substance for the prevention of some forms of cancer.

The leading countries in terms of acreage used for tomato cultivation are Italy, Mexico, Egypt and Brazil. The Australian tomato industry in general supports two types of cultivation viz. greenhouse and open-field. All greenhouse-cultivated tomatoes are marketed as fresh produce, while 85% of the open-field tomatoes are processed into tomato puree. This tomato puree forms the base for manufacture of many other marketable tomato products. Australian exports and imports of processed tomato products have increased steadily over the past five years. The products that have increased significantly are processed tomato sauces and ketchups and tomato/paste puree products. This shows a change in eating habits and also shows that processed tomato products are in demand.

The traditional process of conversion of raw tomato fruit into puree involved the use of atmospheric thermal evaporation, which was quite detrimental to heat sensitive food components. The introduction of multi-effect evaporators operating under vacuum has seen an improvement in product quality. However, current thermal vacuum evaporation processes still have some disadvantages such as the loss of colour and volatile flavour in the final tomato concentrates. Furthermore, in terms of energy expenditure, thermal vacuum evaporation processes consume more energy than other more recent concentration techniques.

Membrane concentration processes such as ultrafiltration and reverse osmosis and isothermal membrane distillation, which operate at lower temperatures than thermal evaporation processes, can be used as alternative methods for concentration of tomato juice. Some of the main advantages of these membrane

processes include increased juice yield/recovery, enhanced product quality, cold sterilization for cold packaging, low energy requirements, minimum waste production, and possible by-product recovery. The use of hydrophilic membrane processes such as UF and RO has been well documented, however, the use of hydrophobic membrane processes such as IMD has not been investigated in detail for juice processing, and particularly for juices, such as tomato, which contain particulate matter.

IMD is a patented membrane process that can be used for the concentration of fruit and vegetable juices. This process operates at ambient temperature and low pressures hence preserving the heat and pressure sensitive food components. The current commercial use of the IMD process is in the wine industry where it is effective for the concentration of clarified grape juice for winemaking. Membrane materials currently available for the IMD process are restricted to processing only clarified feeds. For this reason particulate juice has to be fractionated prior to concentration by IMD. Although the membrane material can be a limiting factor, the benefits of obtaining tomato concentrates of better sensory qualities such as colour and flavour surpasses this current setback.

CHAPTER 3

Materials and Methods

3.1. Collection and preparation of commercial varieties of tomatoes and tomato juice

Salad varieties of Roma tomatoes were used for the initial phase of this study because processing varieties were only available during a limited period each year. The salad varieties of tomatoes were obtained from Safeway supermarket (Werribee, Victoria) and most of the methodology and processing techniques were developed using these tomatoes. The results of the work with salad varieties have not been reported in this study. Two processing varieties, Alta and UC82B were obtained from Heinz Watties Australasia (Victoria) and Unifoods (Victoria), two commercial processors of tomato products. Processed tomato juice prepared at two different break temperatures was obtained from Berrivale Ltd. (South Australia), a commercial fruit juice processor.

3.1.1. Problems encountered during sample collection

The commercial varieties studied were difficult to obtain during the early stages of the project due to seasonal inaccessibility. This problem was mainly encountered with the Alta variety and is the reason for the absence of some compositional data on this variety in the second processing season. There was also initial difficulty in matching processor codes with specific varieties since most of the processors used codes rather than varietal names. For this reason some of the tomatoes were obtained directly from the growers.

3.1.2. Storage of tomatoes for future enzyme studies

Tomatoes were washed and blotted dry with paper towel and then stored at the temperatures shown in Figure 3.1. The stored fruits were later used for enzyme studies after subsequent thermal inactivation of enzymes.

3.2. Thermal inactivation of enzymes

Tomatoes were removed from storage and processed as indicated in Figure 3.2. Approximately 250 g of tomatoes were sliced and then blended using a blender (Model 7011; Waring, CT., U.S.A.) for 1 min intervals at 4°C to produce tomato pulp. Pulp samples, each 50 g in weight, were transferred to 200 mL flasks for enzyme inactivation studies.

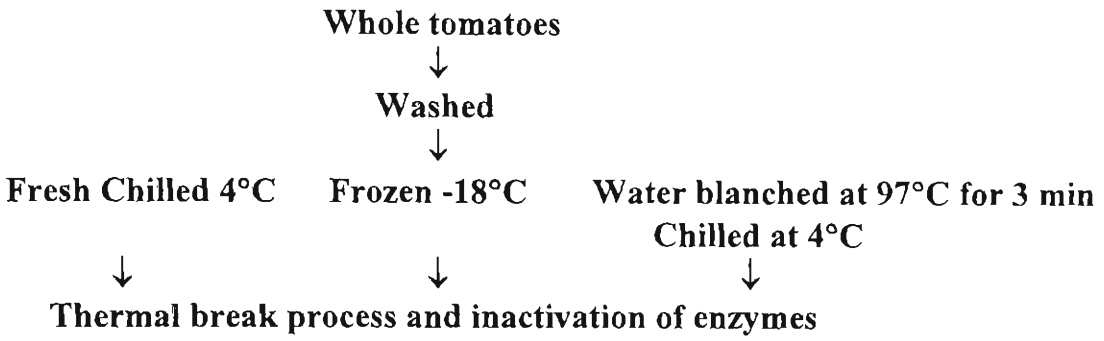


Figure 3.1 Flow diagram of pre-treatment of tomatoes prior to thermal inactivation

Thermal inactivation studies were carried out according to the method of Nath and Ranganna (1977) using the time and temperature conditions indicated in Figure 3.2. The samples were thermally treated in a shaking water bath (Model SS40-A5; Grant, Cambridge, England) and process temperatures were monitored using an electronic thermometer (Model E-93400-00; Cole Palmer, Ill., U.S.A.). After thermal treatment, the tomato pulp samples were immediately cooled to 4°C by immersion and shaking in a pre-chilled water bath. Tomato juice was prepared from the cooled heat-treated pulp by processing it through a tomato press (Master press, Rome, Italy) to remove the seeds and skin. Enzyme extracts were prepared from the thermally treated juice samples as described in Section 3.2.1.1.

3.2.1. Enzyme assay

Tomatoes were removed from storage and processed as indicated in Figure 3.2. The residual activity levels of the three deteriorative enzymes, peroxidase (PO), pectinmethylesterase (PME) and polygalacturonase (PG) were measured in the prepared enzyme extracts.

Samples of chilled, frozen (thawed) and blanched (cooled) tomatoes

↓ **Blended at 4°C**

Tomato pulp

↓**Thermal break process** (65, 75, 85 and 95°C for 2, 4, 6, 8 and 10 min)

Heat-treated pulp

↓ **Cooled to 4°C and removal of seeds and skin**

Tomato juice

Figure 3.2 Flow diagram of thermal inactivation of tomato pulp

3.2.1.1. Preparation of enzyme extract

Tomato juice was centrifuged at 12,000 x *g* for 15 min at 4°C. The supernatant was filtered through a Whatman number 3 filter paper and the filtrate (enzyme preparation) was collected in Eppendorf tubes. The enzyme extract was immediately stored at 4°C pending use in enzyme assay studies, which were carried out within 24 hours of extraction.

3.2.1.2. Peroxidase enzyme

PO activity was determined according to the method of Stauffer (1986). The enzyme activity was initiated by the addition of 100 μL of enzyme extract to 2.9 mL of the reaction mixture in a 10 mm path length cuvette. The reaction mixture contained 125 μg of pyrogallol (Sigma-Aldrich, MO., U.S.A.) and 0.4 mL of 3% (w/w) hydrogen peroxide and was made up to 50 mL in 0.1 M phosphate buffer at pH 7.0. Blanks were prepared using all the reagents except the enzyme extract. The change in absorbance was measured at 430 nm for 1 min at 30°C using an UV/visible spectrophotometer (Cary Model 1E; Varian Instruments, TX., U.S.A.) equipped with a thermostated cuvette holder. The final result was the average of three replicates and the PO activity was reported as the change in absorbance/min/mL in the juice. The reported results were statistically analysed using a one-way analysis of variance (ANOVA) test at $P \leq 0.05$.

3.2.1.3. Pectinmethylesterase enzyme

PME assay was carried out by the method of Hagerman and Austin (1986). The reaction cuvette contained 2 mL of 0.5% (w/v) citrus pectin solution (Sigma-Aldrich, MO., U.S.A.) at pH 7.0, 0.01% (w/v) bromothymol blue in 0.003 M phosphate buffer (pH 7.5) and 0.83 mL of distilled water (pH 7.5). Blanks were prepared using all the reagents except the enzyme extract. The reaction was started by the addition of 10 μL of enzyme extract and the absorbance was recorded at 620 nm for 1 min at 30°C using a UV/visible spectrophotometer (Cary Model 1E; Varian Instruments, TX., U.S.A.) with thermostated cuvette holder. The PME activity was reported as μmoles galacturonic acid equivalents/min/mL in the juice sample and this final result was the average of three replicates. Statistical variation was analysed using a one-way ANOVA test at $P \leq 0.05$.

3.2.1.4. Polygalacturonase

PG activity was measured according to the method of Marangoni *et al.* (1995). The reaction mixture contained 100 μL of enzyme extract, 0.2 mL of 0.1 M sodium acetate (pH 4.5) and 0.2 mL of sodium chloride. The reaction was initiated by the addition of 0.5 mL of 1% (w/v) polygalacturonic acid (Sigma grade III, Sigma-Aldrich, MO., U.S.A.) at pH 4.5. The samples were incubated at 37°C for 30 min. Control (blank) samples were heated for 5 min at 95°C. The liberated glucose groups were measured spectrophotometrically at 520 nm (Novaspec II, Pharmcia Biotech, New Jersey, U.S.A.) according to the arsenomolybdate method of Nelson (1944). The final PG activity was the average of three replicates and was reported as nmoles galacturonic acid reducing group equivalents/min/mL of juice sample. The reported results were statistically analysed using a one-way ANOVA test at $P \leq 0.05$.

3.2.2. Calculation of thermal process schedule for tomatoes

The process temperatures and times of inactivation of each enzyme were recorded. The thermal inactivation time (TIT) curve and thermal resistance time (TRT) curve were plotted using the method outlined by (Ranganna, 1986).

Plotting the TIT Curve

As there was an unavoidable delay in bringing the contents of the thermal inactivation tubes to the required temperature (come-up time), a correction had to be made to the thermal inactivation time. The thermal inactivation time (TIT) graph was plotted on semi-log graph paper using temperature on the linear scale and time on the log scale. The next step involved the plotting of the heat penetration (HP) curve. This was done by plotting time in seconds on the x-axis and temperature on the y-axis on coordinate graph paper. The thermal inactivation rate (TIR) curve was then plotted by finding the thermal inactivation time that corresponded to the various temperatures (from TIT graph), calculating the inactivation rate expression by 1/TIT and plotting the TIR curve on the same graph as the HP curve. The effectiveness of the heat process was determined by:

$$\frac{\text{Area under the TIR curve}}{\text{Area under the HP curve.}}$$

The TIT was corrected by: Correction = Come-up time (1- effectiveness). From this the corrected TIT = Experimental TIT – correction. The corrected TIT was then plotted on a semi-log graph with temperature on the linear scale and time on the log scale.

Plotting the TRT Curve

The same temperatures that were used for the TIT were used for this graph. This graph is similar to the thermal death time curve of bacteria. The temperature was plotted on the linear scale and the D-value on the log scale. Similar corrections were made for the heating lag during the come-up time. The resultant TRT curve was plotted on the same graph as the TIT. The D value (decimal reduction time) was determined from the thermal resistance graph and expressed as a function of the z value at a particular temperature:

$$D = X^{\frac{z}{t}}$$

where, z is the number of °C required to achieve a 10-fold change or 1 log cycle change in thermal inactivation,
t is the temperature of the process (°C), and
X is the D value in min

The F value (total inactivation time) was determined from the thermal inactivation graph and also expressed using the z value at a particular temperature:

$$F = Y^{\frac{z}{t}}$$

where, z is the number of °C required to achieve a 10- fold change or 1 log cycle change in thermal inactivation,
t is the temperature of the process (°C), and
Y is the F value in min

3.3. Physical and chemical analyses of tomato juice

Most of the physical and chemical tests performed in this study were based on those used routinely by the tomato processing industry for monitoring the quality of tomato products. Some of these tests, such as soluble solids content (°Brix) and acidity levels, are used quite early in the processing chain because they are used as indicators of maturity and ripeness and can inform the processor if the crop is ready for harvesting. The physical analyses involved the measurement of properties such as colour, consistency and viscosity. The chemical analyses involved measurement of compositional parameters such as pH, titratable acidity, soluble solids content, suspended solids content, total solids content, sugars (glucose and fructose contents) and hydroxymethylfurfural content. The reported results were statistically analysed using a one-way ANOVA test at $P \leq 0.05$.

3.3.1. Physical analyses

Colour and viscosity measurements were carried out on raw tomato juice and thermally treated juice samples prepared as described in Section 3.2. Consistency measurements were made on the final tomato pastes prepared by linked membrane processes and on commercial concentrates purchased from the supermarket.

3.3.1.1. Colour

Colour measurements were done using a chromameter (Model CR 300; Minolta, NJ., U.S.A). The results were reported as L* a* b* values where L* is the lightness value (0 = blackness, 100 = whiteness), a* is the redness (+ve) or greenness (-ve) and b* is the yellowness (+ve) and blueness (-ve). The reported values for colour were the average of three readings per sample.

3.3.1.2. Consistency

The consistency of paste samples was determined by measurement of the flow of the tomato paste at 20°C using a Bostwick consistometer. The samples were equilibrated at this temperature for 5 hours prior to measurement of consistency. The consistency was indicated by the distance (cm) travelled by the sample under its own weight in a 30 second period. The reported results were the mean of three readings.

3.3.1.3. Viscosity

The juice and concentrate viscosity, expressed as millipascals per second (mPa.s), was measured at 20°C with a Brookfield viscometer (Model DV-II, Brookfield Engineering Labs, Inc., MA., U.S.A.) using spindles LV1 and LV2 at a spindle rotation setting of 12 rpm. All samples were equilibrated at the test temperature for an hour prior to measurement. The viscometer was calibrated by standardization against a paraffin standard of 12,500 mPa.s. The final viscosity reading was an average of three independent measurements.

3.3.2. Chemical analyses

Fresh, frozen and blanched tomato juice samples were analysed both before and after thermal treatment. The juice was prepared as shown in Figure 3.2. The pH, titratable acidity, soluble solids and total solids were routine tests done on the processed juice samples, the juice serum obtained during linked membrane processing and the final tomato pastes. The suspended solids and sugar contents were determined only on MF, UF and RO processed juice serum. The ascorbic acid and HMF contents were measured in the final tomato pastes prepared by linked membrane processes and in the commercial tomato pastes used for sensory analysis.

3.3.2.1. Ascorbic acid content

The ascorbic acid content of the paste samples was determined according to the titration method of Kimball (1991). The paste samples were diluted 1:10 with distilled water and 10mL of the diluted sample was used for the assay. A 0.1%

(w/v) L-ascorbic acid standard (Sigma-Aldrich, MO., U.S.A.) was used and the results were reported as mg/100mL and were the average of three readings.

3.3.2.2. HMF content

The HMF contents of the experimental and commercial tomato pastes were determined according to the HPLC method of Porretta and Sandei (1990) with some minor modifications. Paste samples (10g) were diluted with 40g of water prior to clarification by the addition of Carrez I and II reagents ((Sigma-Aldrich, MO., U.S.A.). Clarified sample (10μL) was isocratically eluted with 90:10 v/v water:methanol solution (water: Milli-Q, Millipore CPMQK05R1, Amicon, Australia; methanol: HiperSolv HPLC grade, Sigma-Aldrich, MO., U.S.A.) at a flow rate of 1.5mL/min at 65°C. The HPLC system comprised an autosampler (Model 9100, Varian Instruments, TX., U.S.A.), a solvent delivery system (Model 9010, Varian Instruments, TX., U.S.A.) and an ultraviolet detector operating at 285nm (Model 9050, Varian Instruments, TX., U.S.A.). The column used for the assay was a reverse phase C-18 radial pack of 250mm length and 4mm internal diameter with a mean particle diameter of 10μm (Model Ultracarb 5 ODS/30, Phenomenex, Sydney, Australia). The HMF (0.1 % w/v) standard stock solution (Sigma-Aldrich, MO., U.S.A.) was prepared in 90:10 water:methanol mixture and eluted under the same conditions as that used for the paste samples. The results were reported as ppm of HMF and were an average of three replicates.

3.3.2.3. pH

The pH of tomato juice was measured at 20°C using a pH meter (Model 100 - Cyberscan; Cole Palmer, Ill., U.S.A.). The reported results were the mean of three readings of triplicate samples.

3.3.2.4. Soluble solids

The soluble solids level was measured at 20°C using a refractometer (Model N-20; Atago, Tokyo, Japan) and reported as °Brix. The reported results were the mean of three readings.

3.3.2.5. Sugars - glucose and fructose contents

The glucose and fructose contents of the RO permeate were determined using an HPLC method purposely created for this study. The HPLC system comprised an autosampler (Model 9100, Varian Instruments, TX., U.S.A.), a refractive index (RI) detector (Model 9040, Varian Instruments, TX., U.S.A.), a solvent delivery system (Model 9012, Varian Instruments, TX., U.S.A.) and a column heater (Model 330, Altech, TX., U.S.A.). Prior to loading on the HPLC, all samples were filtered using a 0.45 μm disc filter. Samples (15μL) were eluted using a carbohydrate column (Aminex HPX-87P, Bio-Rad, CA., U.S.A) of 300 mm length and 7.8 mm internal diameter. The liquid phase was Milli-Q treated water at a flow rate of 0.6 mL/min and at a temperature of 80°C. The glucose and fructose (Sigma-Aldrich, MO., U.S.A.) standard solutions (0.1% w/v) were prepared in Milli-Q treated water. The final reported results were the average of three measurements.

3.3.2.6. Suspended solids content

The suspended solids content was determined according to the procedure of the Association of Official Analytical Chemists (AOAC, 1990) with slight modifications. Juice sample (20 g) was accurately weighed and mixed thoroughly with approximately 30 mL of hot distilled water. The mixture was cooled and centrifuged at 20,000 x *g* at 25°C. The mixture was filtered under suction in a Buchner funnel using a previously dried (at 100°C for 2 h) Whatman number 3 filter paper. The filter paper was transferred to a moisture dish and dried in a vacuum oven (Model OUL 570 010J, Sanyo-Gallenkamp, Osaka, Japan) for 3 h at 80°C and then cooled in a desiccator and weighed. The results were reported as percent of total suspended solids and were the average of three measurements.

3.3.2.7. Titratable acidity

The free acid was determined by weighing 10 g of sample into an Erlenmeyer flask, diluting with 50mL of distilled water, adding 5 drops of phenolphthalein indicator (1% w/v solution in ethanol) and titrating against a 0.1N NaOH solution to a faint pink colour. For tomato pastes, since the end-point was harder to detect

visually, the test solution was titrated until a pH of 8.1 was reached using a pH meter (Model 100 - Cyberscan; Cole Palmer, Ill., U.S.A.).

The results, calculated using the following equation, were an average of three determinations and were reported as g/100g of citric acid:

$$a = \frac{b \,.c.\, d \,.e \times 100}{f}$$

where, a = % acidity
b = titre (mL)
c = normality (N)
d = volume made up (mL)
e = equivalent wt of citric acid (g)
f = wt of sample weighed (g)

3.3.2.8. Total solids content

The total solids content was determined using the method described by Luh and Daoud (1971) with some modifications. For tomato paste only 5 g of sample was used instead of 12 g as used for juice. Approximately 10-15 g of distilled water was added to the tomato paste and mixed well before oven drying. The samples were dried in a vacuum oven (Model OUL 570 010J, Sanyo-Gallenkamp, Osaka, Japan) at 70°C under 500 mPa pressure until a constant weight was obtained. The results were an average of three replicates and were reported as the percent total solids.

3.4. Microbiological analyses

The test samples were diluted according to the method described in Australian Standard AS 1766.1.2 (Standards Association of Australia, 1991). Tomato juice/serum was diluted by the addition of 10 mL of sample to 90 mL of sterile peptone water and tomato paste was diluted by addition of 10 g of sample to 90mL of sterile peptone water. Sample aliquots of 0.1 mL of 10^{-1} to 10^{-6} dilutions were used for the analyses. Statistical variation was analysed using a one-way ANOVA test at $P \leq 0.05$.

3.4.1. Total count

The total microbial count was determined using the pour plate method detailed in Australian Standard AS 1766.2.1 (Standards Association of Australia, 1991). The plates were incubated at 30 ± 1°C for 48 ± 3 h and the results were reported as colony-forming units (cfu)/mL for the juice samples and cfu/g for the paste samples and were the average of three replicates.

3.4.2. Yeast and mould count

The yeast and mould counts were determined by the pour plate method described in Australian Standard AS 1766.2.2 (Standards Association of Australia, 1991) using oxytetracycline glucose yeast extract agar. The plates were placed upright and incubated at 25 ± 1°C for 5 days. The counts were an average of three readings and were reported as cfu/mL for the juice samples and cfu/g for the tomato paste samples.

3.4.3. Howard mould count

Although the Howard mould count (HMC) can be determined by different methods, the method obtained from Unifoods (Tatura, Victoria) was used for this study. This method was used because it was less expensive and simpler in terms of analytical procedures. The sample was diluted with distilled water to a soluble solids level between 7.8 and 8.8 °Brix and a drop of diluted sample was placed on a clean Howard Mould slide. The sample was examined under a microscope and 25 fields were systematically checked for mould filaments. A field was reported as positive if not more than three mould filaments exceeded one-sixth the diameter of the field. Branched filaments were considered overall as single filaments in terms of length. If the positive fields varied by more than two, then further slides were prepared until an agreement was reached. Five slides were prepared and the reported results were the average of five separate examinations. All positive fields were reported as a percentage of the HMC. The average HMC reported was a result of three sample replicates, which was a total of fifteen separate examinations for each sample. According to the Australian standards the

maximum legal standard for HMC is 50%. However, the industry limit is usually set at 40% since processing generally increases the HMC by 10%.

3.4.4. *Bacillus coagulans*

Bacillus coagulans was determined by the method of Segmiller and Evancho, (1992). Enumeration was performed using dextrose tryptone agar with bromocresol purple. Since this media can support the growth of *Bacillus stearothermophilus*, the samples were thermally treated to destroy *B. stearothermophilus*. However, when both organisms are present, the individual colonies can be easily identified since *B. coagulans* colonies appears as yellow to orange colonies with a slightly convex shape and fluffy edges whereas *B. stearothermophilis* colonies appear as brown and very small colonies. Any doubtful colonies were confirmed on thermoacidurans agar since *B. stearothermophilis* does not grow at pH 5.0. The samples were incubated at 55 ± 1°C for 48 ± 3 h and the results were reported as an average of three replicates and expressed as cfu/g or cfu/mL.

3.4.5. Coliforms and *Escherichia coli*

The Coliforms and *Escherichia coli* (*E. coli*) were determined by the triplicate tube method as detailed in Australian Standard AS 1766.2.3 (Standards Association of Australia, 1987) and the technique of most probable number (MPN) detailed in Australian Standard AS 1766.1.6 (Standards Association of Australia, 1991) was used to report the results. The tubes were prepared using lauryl tryptose broth and incubated at 37 ± 1°C for 48 ± 3 h. The positive results were reported as MPN/mL for juice and MPN/g for paste samples and were an average of three measurements.

3.5. Clarification of tomato juice and tomato serum

Clarification of tomato juice was carried out in two stages as shown in Figure 3.3. The first stage involved centrifugation to separate the tomato solids from the serum component. The second stage involved further clarification of the serum using the membrane processes of microfiltration (MF) or ultrafiltration (UF). This

secondary clarification was necessary because the serum was to be subsequently concentrated by reverse osmosis (RO) and isothermal membrane distillation (IMD) with the latter requiring clarified feeds for effective operation. The reported results were statistically analysed using a one-way ANOVA test at $P \leq 0.05$.

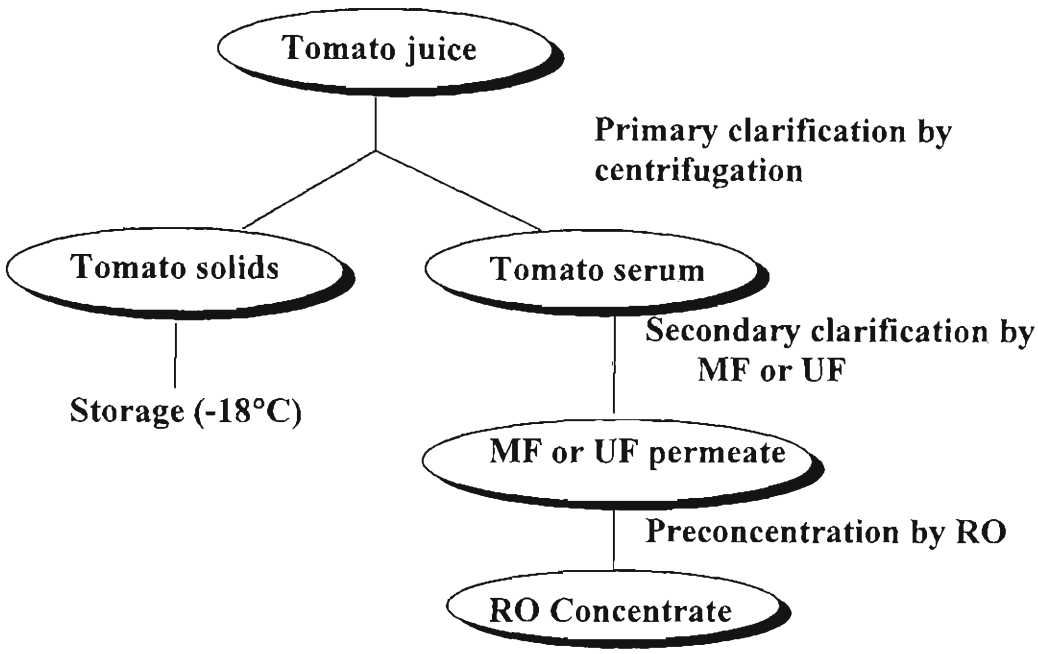


Figure 3.3 Primary and secondary clarification and preconcentration of tomato juice

3.5.1. Primary clarification by centrifugation

Tomato juice from two processing varieties Alta and UC82B were heated at two break temperatures of 85°C and 95°C. The two temperatures were chosen to investigate if there were any benefits in using a lower break temperature. Tomato juice was weighed in 450 g lots and centrifuged at 12,000 x *g* for 30 min at 4°C. The serum fraction was decanted through a miracloth (pore size 22-25 μm, Calbiochem, CA., U.S.A.) to remove any remaining suspended particles. The solid fraction was thermally treated at 95°C for 10 min using a 1000W microwave oven (Panasonic Model MN6755, Matsushita Electric Industrial Co. Ltd., Osaka, Japan) and stored below -18°C pending further use. MF and UF processes further clarified the separated serum. Serum soluble solids, suspended solids, total solids

contents, pH and titratable acidity were determined as described in Sections 3.3.2.4, 3.3.2.6, 3.3.2.8, 3.3.2.3 and 3.3.2.7 respectively. The viscosity was measured at 20°C as described in Section 3.3.1.3.

3.5.2. Secondary clarification by microfiltration and ultrafiltration

Further clarification of tomato serum was achieved by either MF or UF processes using the membrane processing equipment (Model DC10L/ DC10LA, Amicon, MA, U.S.A.) shown in Figure 3.4. The same equipment was used for both MF and UF processes but with different membrane modules as appropriate. The characteristics of the MF and UF membrane modules used (Models H5P01-43 and H5P100 respectively, Amicon, MA, U.S.A.) are given in Table 3.1. Tomato serum, clarified by centrifugation, was processed using the processing conditions listed in Table 3.2. The processing temperature was monitored using an electronic thermometer (Model E-93400-00; Cole Palmer, Ill., U.S.A.). The pressure was monitored using the dial gauges on the plant itself. Permeate samples were collected for a minute at 10 min intervals.

The membrane performance was measured by calculating the flux rate using the following formula:

$$\text{Flux rate} = \frac{\text{Volume of permeate (L)}}{\text{Membrane area (m}^2\text{) x Time (h)}}$$

The MF and UF permeates were analysed for pH, titratable acidity, sugar, soluble solids, suspended solids and total solids contents using the methods outlined in Sections 3.3.2.3, 3.3.2.7, 3.3.2.5, 3.3.2.4, 3.3.2.6 and 3.3.2.8 respectively. The viscosity was measured according to the method described in Section 3.3.1.3.

The MF and UF modules were cleaned using 1% (w/v) P3 Ultrasil 56 (Ecolab, Vic., Australia) and sanitized using 0.1% (w/v) acidified sodium metabisulphite (Divos NBS, Diversey Lever Australia Pty. Ltd., NSW, Australia).

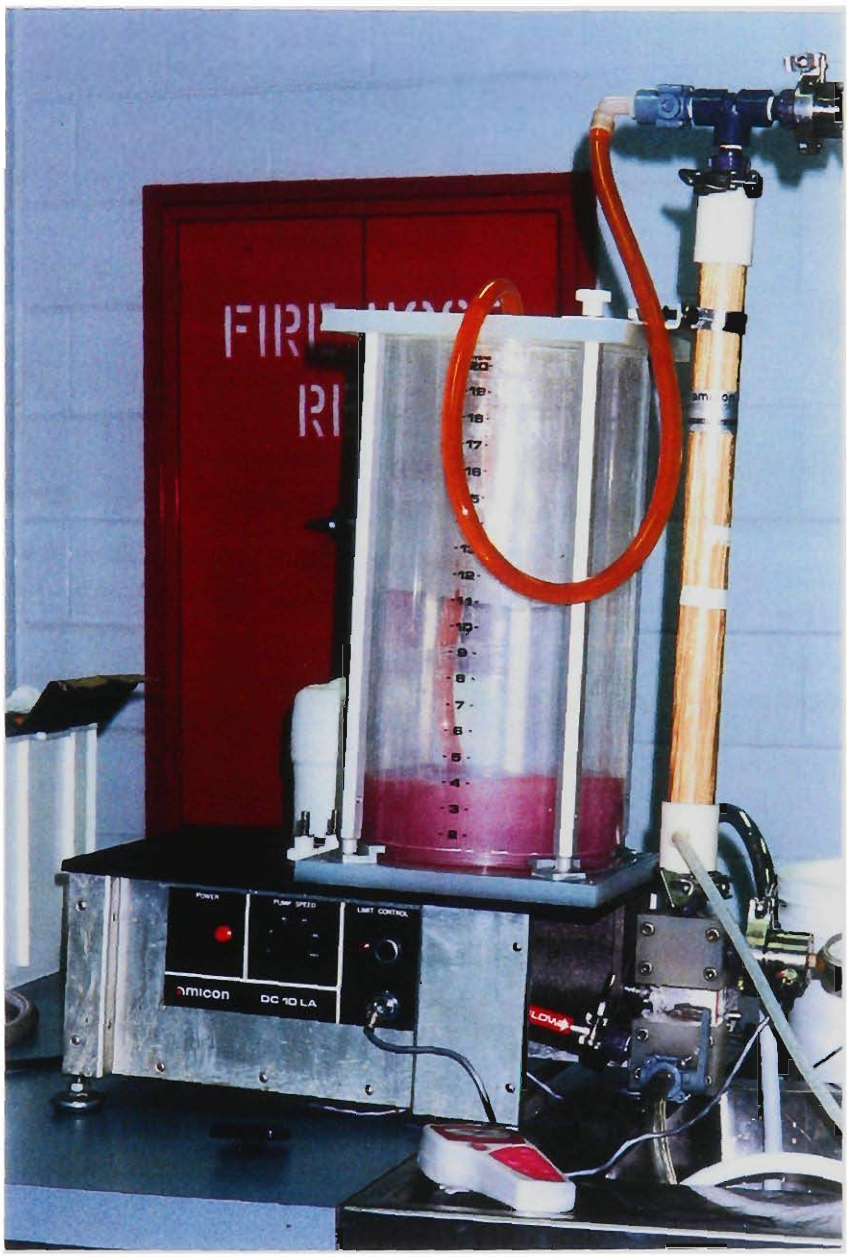


Figure 3.4 **Ultrafiltration system used for secondary clarification of tomato serum**

Table 3.1 Characteristics of the MF and UF modules used in tomato juice clarification

Process	Module Type	Membrane Material	Membrane Area (m^2)	Mean Pore Size (μm)
MF	hollow fibre (H5P01-43)	Polysulfone	0.45	0.1
UF	hollow fibre (H5P100)	Polysulfone	0.45	0.001

Table 3.2 Processing conditions used during MF and UF treatment of tomato juice serum

Processing Parameter	Condition
Temperature (°C)	40
Inlet pressure (kPa)	100 - 130
Outlet pressure (kPa)	25 - 35
Pre-filter size (μm)	150
Samples processed	85°C and 95°C break temperatures
Sample quantity (L)	10

3.6. Preconcentration of tomato serum by RO

Tomato juice permeates prepared by centrifugation and MF/UF processes as described in Sections 3.5.1 and 3.5.2 were preconcentrated by reverse osmosis. The laboratory scale RO plant (Model 2521/AA series, Applied Membrane Inc., CA., U.S.A.) used for the trials is shown in Figure 3.5. The characteristics of the RO element (Model BW30-2521, Dow Chemical Co., U.S.A.) used for the study and the conditions of processing are summarised in Table 3.3. The flux rate ($L.m^{-2}.h^{-1}$) was measured every 10 minutes and calculated according to the equation for flux rate given in Section 3.5.2. The pH, titratable acidity, soluble solids, suspended solids and total solids contents of the RO concentrates and permeates were measured using the methods described in Sections 3.3.2.3, 3.3.2.7, 3.3.2.4, 3.3.2.6 and 3.3.2.8 respectively. Sugars (glucose and fructose) were measured using the HPLC method described in Section 3.3.2.5. The RO permeate was discarded and the RO concentrate was concentrated further by the IMD process. The reported results were statistically analysed using a one-way ANOVA test at $P \leq 0.05$.

Table 3.3 **Membrane characteristics and processing conditions used during RO preconcentration of tomato juice permeate**

Processing Parameter	Condition
Temperature (°C)	10 ± 1
Pressure (kPa)	2000 ± 10
Membrane type	Thin-film composite
Membrane material	Polyamide
Salt rejection of membrane (%)	98
Membrane area (m^2)	1.1
Samples processed	85°C and 95°C break temperatures
Sample quantity (L)	10

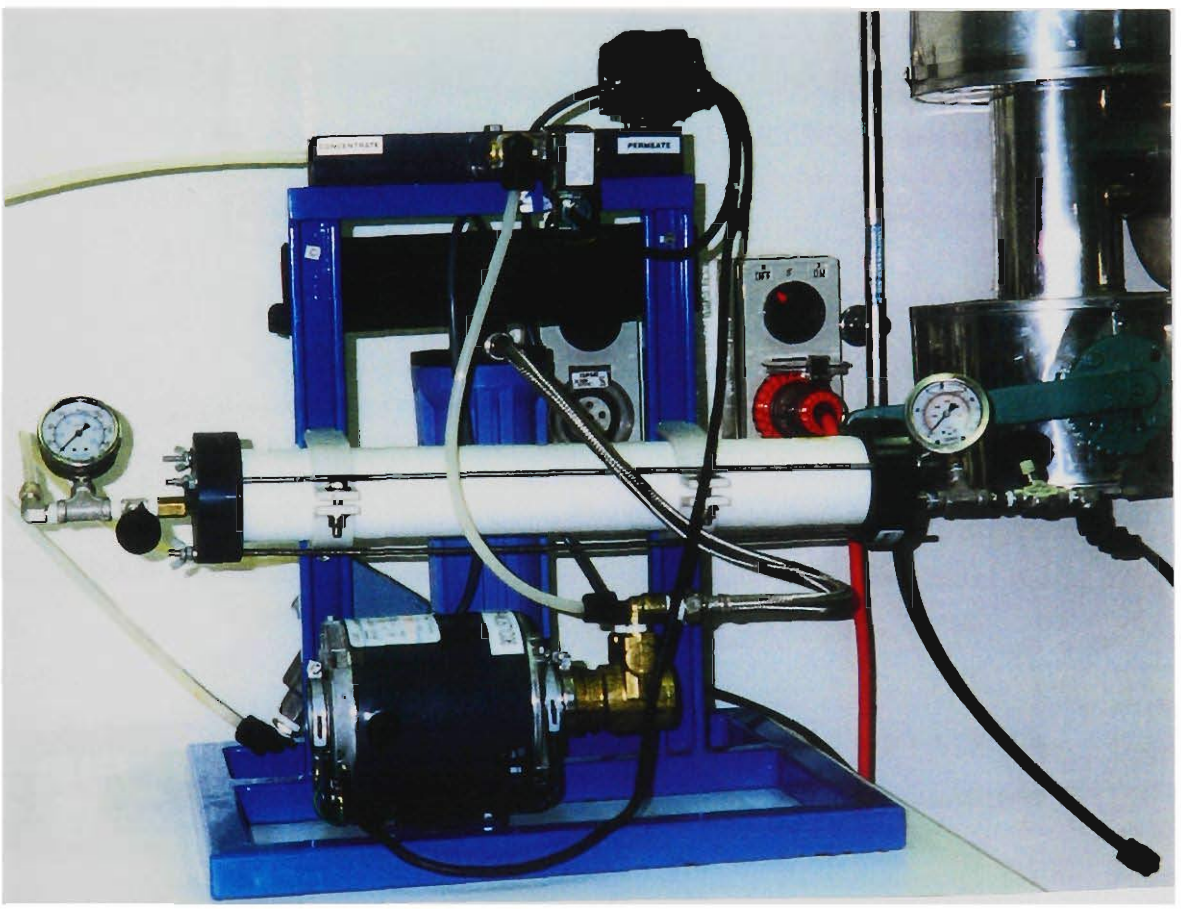


Figure 3.5 **Laboratory scale RO system used for preconcentration of clarified tomato serum**

3.7. Concentration of tomato serum by IMD

The MF or UF clarified tomato serums (ie. permeates) as well as the linked MF/UF clarified, RO preconcentrated tomato serums were further concentrated by the IMD process (Figure 3.6). The IMD system and the individual cell used for further concentration of clarified and preconcentrated tomato serum is shown in Figures 3.7 and 3.8 respectively. The IMD plant was constructed, installed and commissioned as part of this study.

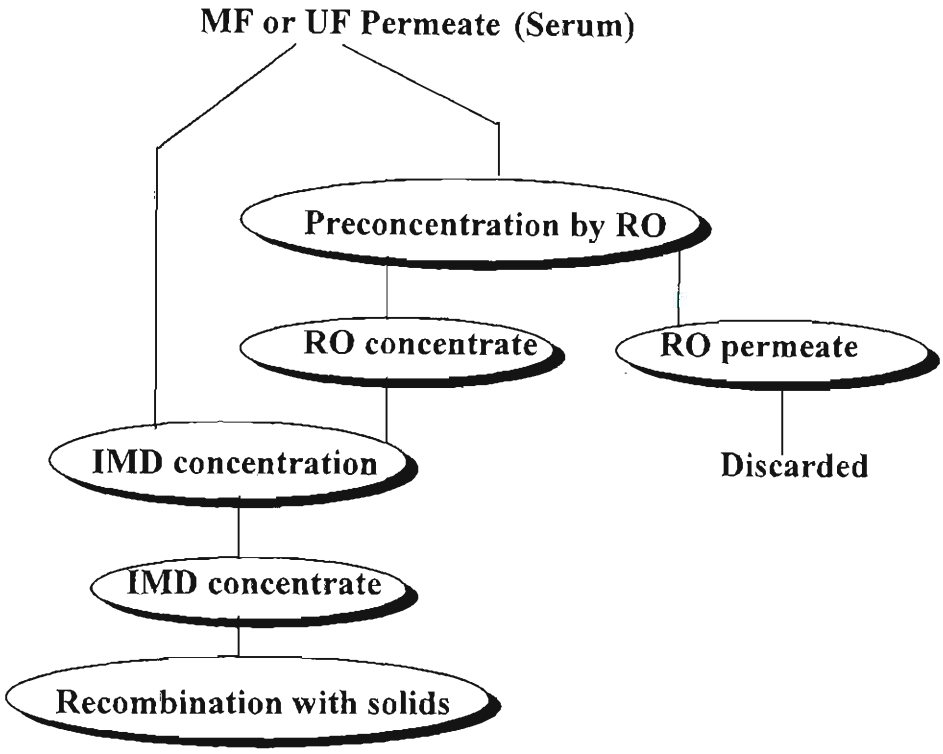


Figure 3.6 IMD Concentration of MF/UF treated tomato serum and linked MF/UF- RO treated tomato serum

3.7.1. Construction, installation and commissioning of the IMD plant

The initial phase of the construction stage was achieved by purchasing individual instruments and components, which are listed in Table 3.4. Most of the parts in contact with the tomato serum were stainless steel. The temperature, pressure and flow devices all had sanitary seals to avoid contamination during processing. This also enabled the system to be cleaned and sanitized in place without tedious dismantling of the plant. The IMD components were mounted on a stainless steel table that was purposely designed for mobility. The IMD plant was built and

initially commissioned at the University of Melbourne, City campus and later at Victoria University of Technology, Werribee campus. A process flow diagram for the IMD plant is illustrated by Figure 3.9, which also shows each individual component of the plant.

Table 3.4 Components used in the construction of the IMD system

Component	Model and Source
IMD cell	Osmonics- Sepa CF, Patent No. 4,846,970, Minn., U.S.A.
Peristaltic pump drive	Masterflex L/S 7521-47, Cole Palmer, Ill., U.S.A.
Peristaltic pump head	Masterflex, L/S 77201-62, Cole Palmer, Ill., U.S.A
Temperature device	FIR-201-M, Shinko Technos Co. Ltd., Osaka, Japan
Pressure transmitter	P21, Philips Industrial Electronics, Kassel, Germany
Flowmeter	M5, M^{c}Naught Industries Pty. Ltd., NSW, Australia
Tank stirrers	IKA Labortechnik RW20, Crown Scientific, NSW, Australia
Tanks	5-15L capacity, stainless steel
Pipes	12mm stainless steel
Flexible tubing for pump drive	Masterflex L/S 06409-24, Cole Palmer, Ill., U.S.A.

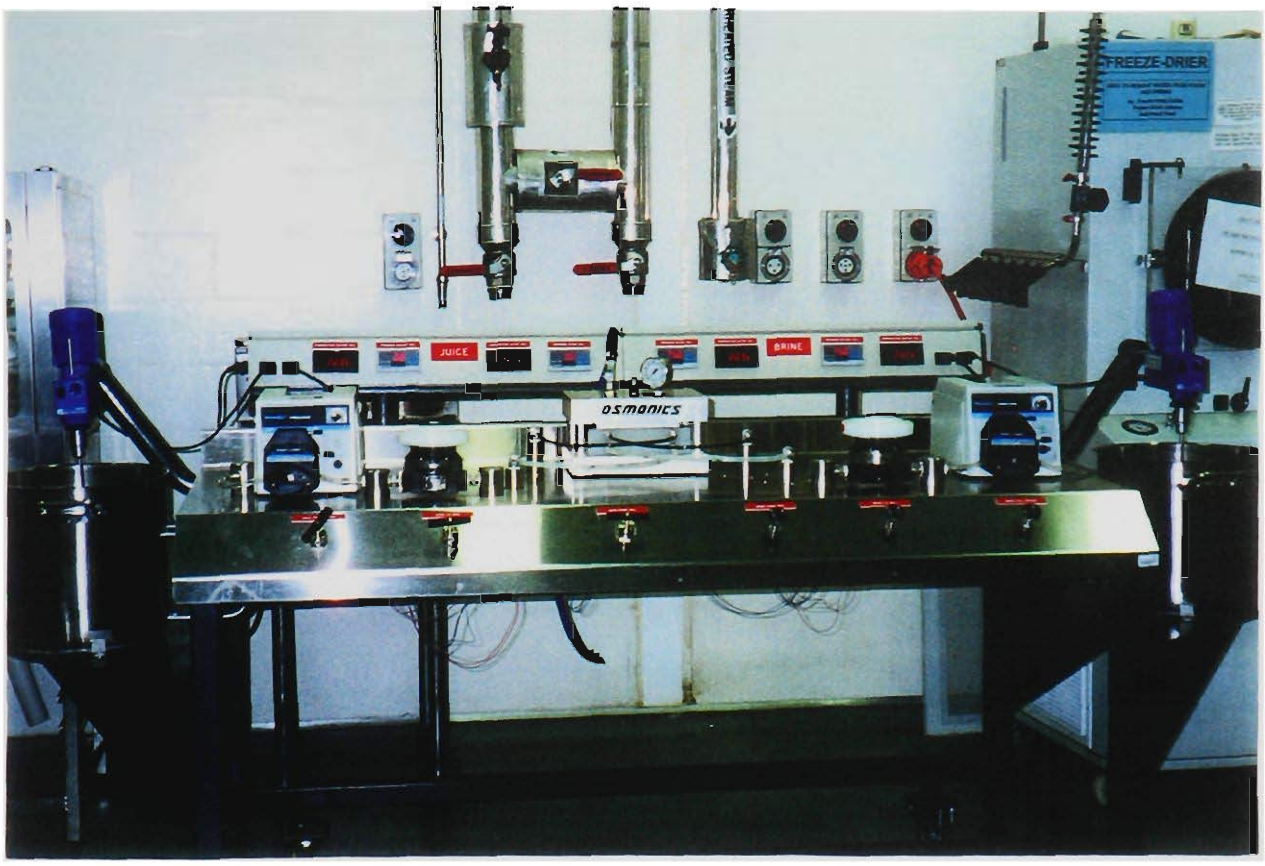


Figure 3.7 IMD system used for concentration of clarified and preconcentrated tomato serums

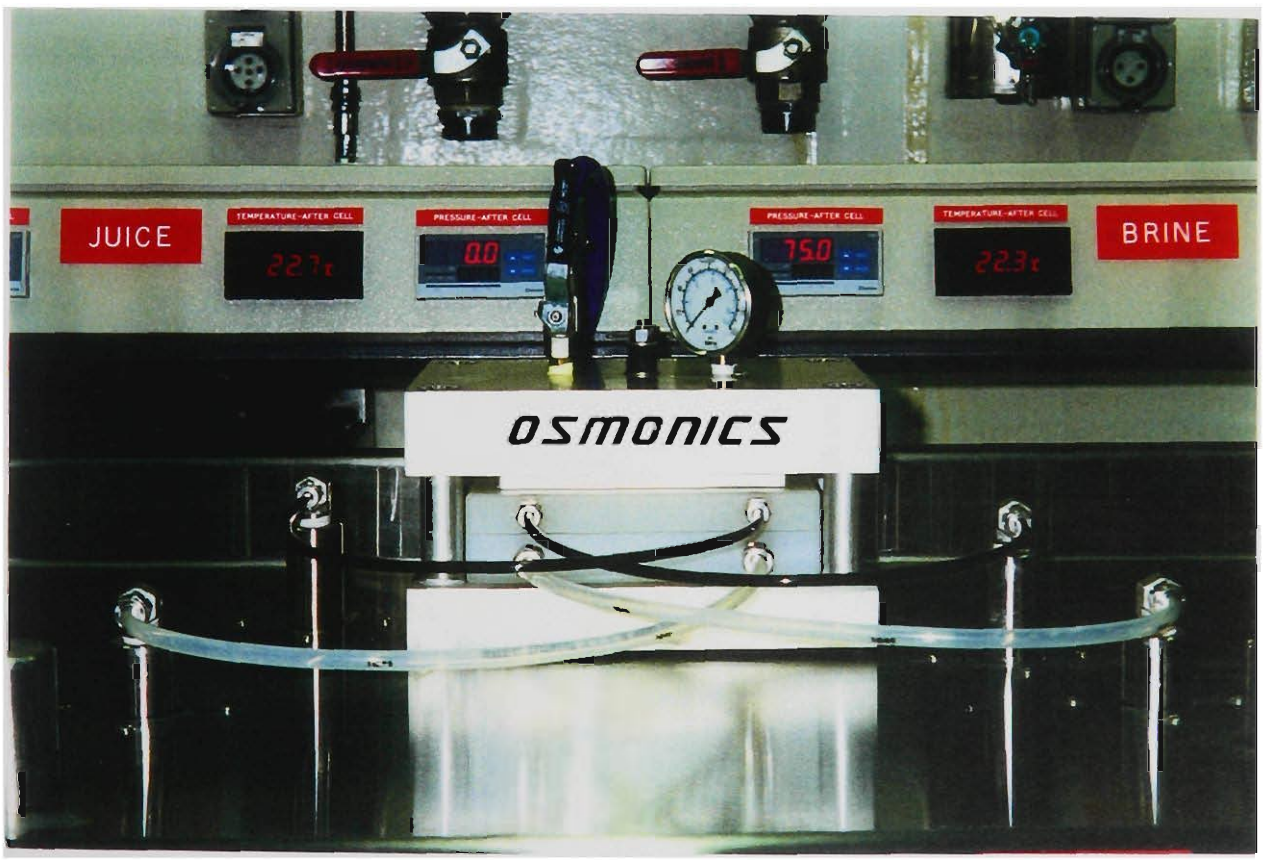
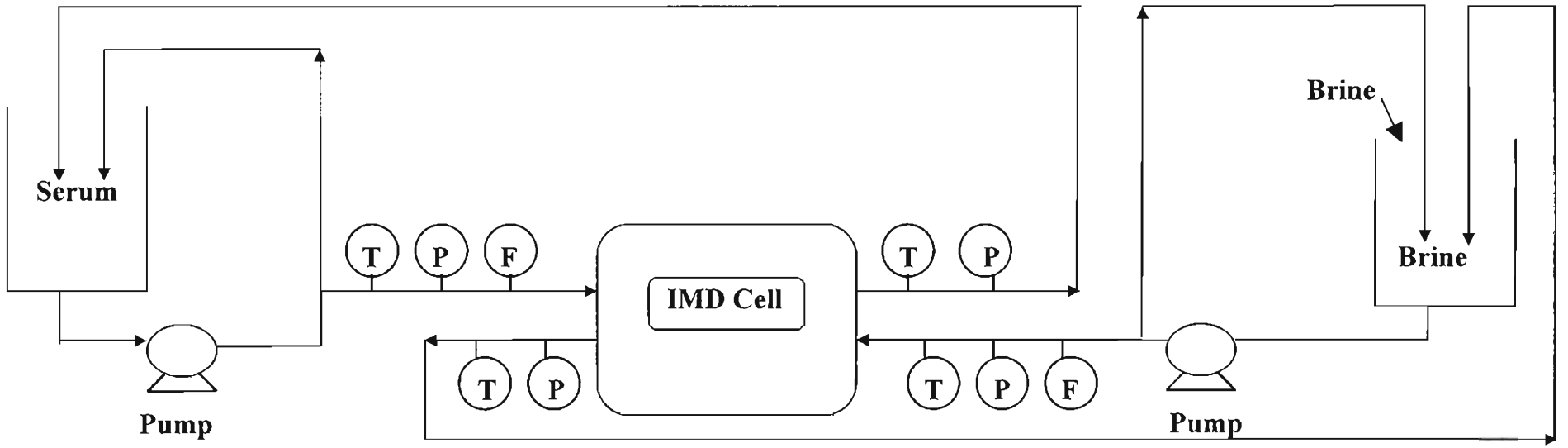


Figure 3.8 Individual IMD cell component used for concentration of clarified and preconcentrated tomato serums



T - Temperature device **P** - Pressure device **F** - Flow device

Figure 3.9 IMD process flow diagram

3.7.2. IMD processing

As mentioned in Section 2, IMD concentration involves two surfaces of the hydrophobic membrane. The juice permeate or serum is passed on one side of the membrane and a concentrated brine solution is passed counter-currently on the opposite surface of the membrane. The differences in osmotic pressure between the juice permeate and the brine solution creates a vapour pressure difference, which results in the transfer of water vapour molecules from the juice into the brine solution. As a result of the water vapour transfer, the brine solution becomes diluted and has to be continuously concentrated so that a saturation point is maintained. In the present study, salt was continuously added to maintain the concentration level of the brine. However, for larger commercial processes a thermal evaporator is used to maintain the concentration of the brine. The choice and concentration of the brine solution is important during IMD concentration and has been discussed previously in Section 2.6.1.8.1. For this study dipotassium orthophosphate (K_2HPO_4) was used for preparation of the brine solution. The concentration of the brine was maintained at 50% (w/w) and the temperature of the brine was thermostatically maintained at 25°C. The types of IMD membranes used for this study are given in Table 3.5. The samples and processing conditions used during IMD concentration are given in Tables 3.6 and 3.7 respectively. The retentate was weighed hourly and the weight loss was noted as the IMD permeate (kg). The membrane performance was determined by calculating the flux rate according to the equation:

$$\text{Flux rate } (kg.m^{-2}.h^{-1}) = \frac{\text{Weight of permeate (kg)}}{\text{Membrane area } (m^2) \times \text{Time (h)}}$$

The membrane that had the highest and most consistent flux rate was selected for subsequent IMD temperature and concentration studies. The reported results were statistically analysed using a one-way ANOVA test at $P \leq 0.05$.

Table 3.5 IMD membranes used for concentration of tomato serum obtained from linked MF/UF-RO processes

Membrane	Material	Nominal Pore Diameter[a] (μm)	Membrane Thickness[b] (μm)
Celgard 2500[1]	Polypropylene	0.12	28
Gelman 2TPR[2]	Fluoroethylene copolymer	0.20	10
Goretex XP 98006[3]	Polytetrafluroethylene	0.20	48
Goretex XP 98007[3]	Polytetrafluroethylene	0.45	50
Sumitomo WP 02-40[4]	Polytetrafluroethylene	0.20	47

[1] Hoechst Celanese Corp., U.S.A
[2]Gelman Sciences Pty Ltd, Australia
[3]W.L Gore & Associates, Australia Pty Ltd
[4] Sumitomo Electric Ind. Ltd, Australia

[a] Manufacturers data
[b] Measured by micrometer

Table 3.6 Samples concentrated by the IMD process

Sample	Description
1	85°C break MF permeate
2	85°C break UF permeate
3	95°C break MF permeate
4	95°C break UF permeate
5	85°C break, linked MF permeate-RO concentrate
6	85°C break, linked UF permeate-RO concentrate
7	95°C break, linked MF permeate-RO concentrate
8	95°C break, linked UF permeate-RO concentrate

Table 3.7 Processing conditions used during IMD concentration of tomato serum obtained from linked MF/UF-RO processes

Variable	Processing Conditions
Temperature of IMD feed (°C)	10 and 25
Temperature of brine (°C)	25 ± 2
Back pressure of IMD feed (kPa)	35 ± 5
Back pressure of brine (kPa)	35 ± 5
Brine type	Dipotassium orthophosphate (K_2HPO_4)
Brine concentration (%w/w)	50
IMD feed flow rate (mL/min)	500
Brine flow rate (mL/min)	450

3.7.3. Cleaning and sanitation of the IMD system

Fouling of IMD membranes affects their hydrophobicity and hence their efficiency. The hydrophobicity of the membranes can be determined by several different methods. The conventional method of measuring the contact angle is still used for determination of hydrophobicity but has some limitations such as measurement of the gradient of the graph of solvent concentration vs surface tension as well as the variations of contact angles for the same material (Franken *et al.*, 1987). Other more recent methods such as liquid entry pressure (LEP) and penetrating drop concentration (PDC) are based on the surface tension of the penetrating liquid and have been used with fewer deviations (Sarti *et al.*, 1985; Durham and Nguyen, 1994). For the present study membrane hydrophobicity was determined according to the PDC method of Durham and Nguyen (1994). The IMD plant was cleaned and sanitized in place. Between trials the plant was stored in 0.1% (w/w) acidified sodium metabisulphite solution (Divos NBS, Diversey Lever Australia Pty. Ltd., NSW, Australia).

3.7.3.1. Cleaning of plant

The UF-RO linked tomato serum from the 95°C break temperature juice was used for the cleaning trials. Ten different cleaning agents viz: distilled water, 1% (w/v) Sodium hydroxide (NaOH), 1% (v/v) Nitric acid (HNO_3), 1% (w/v) NaOH and 1% (v/v) HNO_3, 10% (v/v) commercial pectinase - Vinozym 3XL (Novo Nordisk Ferment Ltd. Switzerland), 5% (w/v) Tide laundry detergent, 1% (w/v) P3 Ultrasil

56, 1% (v/v) P3 Ultrasil 72, 1% (v/v) P3 Ultrasil 75 and 1% (v/v) P3 Ultrasil 91 (Ecolab, Australia) were evaluated for their effectiveness in cleaning soiled selected membrane material (Gortex XP 98007). Five cleaning trials were conducted for each cleaning agent and PDC measurements were made after ten hours of processing. Since 1% (w/v) NaOH solution was found to be the most effective cleaning agent for the selected membrane (Gortex XP 98007), it was subsequently used for the routine cleaning of the plant according to the following regime:

1. Water rinse for 15 min at 40°C, not recirculated.
2. 1% (w/v) NaOH solution rinse for 60 min at 40°C with recirculation.
3. Water rinse for 15 min at 40°C, not recirculated.

3.7.3.2. Sanitation of plant

The system was sanitized by soaking in a 0.1 % w/w sodium metabisulphite solution (Divos NBS, Diversey Lever Australia Pty. Ltd., NSW, Australia) for five hours. All trials, including those using new membranes, were commenced using sanitized membranes and plant.

3.8. Recombination of tomato solids and concentrated serum

The frozen tomato solids fraction and the UF solids (i.e from the secondary clarification process) were thawed at 4°C in a refrigerator for 24 h. The UF concentrate was chosen because the corresponding UF permeate was a better IMD feed than the MF permeate since it gave better flux rates during IMD processing. Two recombined tomato pastes (blends A1 and A2) were prepared by recombining weighed portions of tomato solids, UF concentrate and IMD concentrate to produce recombined tomato pastes of 25 and 30% (w/w) total solids content (Table 3.8). The level of total solids chosen for blend A1 was based on commercial paste levels, however a higher level of total solids was chosen for blend A2 to compare if a higher level of IMD concentrate would impact on sensory properties. The pastes were salted at the 3% (w/w) level to match the salt content of commercial samples. The recombined pastes were then

heated to 90°C using a 1000W microwave oven (Panasonic Model MN6755, Matsushita Electric Industrial Co. Ltd., Osaka, Japan) and then hot filled in pre-sterilized 250 g glass jars. The jars were inverted and cooled to 20°C. Some samples were stored at ambient temperature while others were refrigerated at 4°C. The colour, consistency, ascorbic acid content, HMF, soluble solids, titratable acidity and total solids content of the new pastes was measured according to the methods given in Sections 3.3.1.1, 3.3.1.2, 3.3.2.1, 3.3.2.2, 3.3.2.4, 3.3.2.7 and 3.3.2.8 respectively. Microbiological assessment included testing for total microbial count, yeast and mould count, Howard mould count, *Bacillus coagulans* and *Echerichia coli* and was performed according to the methods outlined in Sections 3.4.1, 3.4.2, 3.4.3, 3.4.4 and 3.4.5 respectively. The experimental pastes were then compared to commercial pastes using sensory taste panels.

Table 3.8 Recombination strategies for the preparation of two recombined blends of tomato pastes

Item (g/100g paste)	Paste A1	Paste A2
Quantity of centrifuged tomato solids at 10.07 % (w/w) total solids	60	45
Quantity of UF concentrate at 5.45 % (w/w) total solids	5	5
Quantity IMD concentrate at 47.2 % (w/w) total solids	33	47
Salt (% w/w)	3	3
Total solids (% w/w)	25	30

3.9. Sensory assessment of tomato pastes

The sensory characteristics of the recombined tomato paste samples were assessed by means of sensory evaluation panels. The experimental paste blends were tested against two leading commercial brands of tomato paste. The paste samples were assessed at room temperature by an untrained panel of 25 panelists. Each paste sample was presented in two forms, as a spoonable concentrate and on a pizza base. Each paste blend was tested on a different day so that the panelists would not become fatigued. The sensory test used to assess the pastes was the

rating test given in Australian Standard AS 2542.2.3 (Standards Association of Australia, 1988) using a 9-point hedonic bipolar scale and was done twice for each sensory parameter. This test was chosen so that the intensity of the preference could be determined rather than a straight rejection or acceptance of the sample. Sample sensory evaluation sheets are shown in Appendices 1 and 2. The panelists were selected from within the university community and the same panelists were used for both of the panel sessions. Statistical comparison of the panel data was made using one-way ANOVA at $P \leq 0.05$. When there was a significant difference, the magnitude of the difference was analysed using Tukey's test (Larmond, 1967), which was based on the difference of sample means.

3.9.1. Comparison of experimental pastes with commercial pastes - straight sampling

Three tomato pastes (1 experimental blend paste and the 2 commercial pastes) were allowed to stand at room temperature for 3 hours prior to assessment by panelists. Approximately 1 tablespoon of each paste was placed on a white plastic plate and presented to each panelist. Water and crackers were served to eliminate any carry-over of flavour. Each paste was assessed for colour, aroma, texture and flavour and scored 1 to 9 with 1 as least preferred and 9 as most preferred. The results were analysed statistically according to the methods stated in Section 3.9.3.

3.9.2. Comparison of experimental pastes with commercial pastes - on a pizza base

Pizza bases were made according to the method described in Section 3.9.4. Each precooked base was divided into three sections and approximately 4 tablespoons of each tomato paste sample was spread evenly on each portion of the base. The base was then heated for 5 minutes at 280°C and then cooled to ambient temperature. The base was then cut up into 5 cm squares and placed on sample plates and presented to the panelists. Three pizza samples were served per panelist. The texture and flavour of the pizza was assessed using a 1 to 9 scale with 1 as least preferred and 9 as most preferred. The results were analysed statistically according to the method stated in Section 3.9.3.

3.9.3. Statistical analysis of sensory evaluation data

One-way analysis of variance (ANOVA) was calculated on the hedonic scores obtained from the panel sessions. The variation between the pastes was reported using ANOVA tables, which listed the source of the variation and the variance ratio (F) for each sensory property. The calculated F value was compared with the standard F value, which was obtained from the variance ratio tables (Sigma Stat 2.03). If the calculated F values were less than the standard F values there was no significant difference detected at a significance level of $P \leq 0.05$. However, if the F value was greater, this showed that there was a significance difference and the magnitude of the difference was analysed using Tukey's test. In addition to the ANOVA and Tukey's test, paired comparison tests were also done using Australian Standard method AS 2542.2.1 (Standards Association of Australia, 1988).

3.9.4. Preparation of pizza base

The pizza base was prepared according to the following recipe: Dried compressed yeast (30 g) and 5 g of sugar were mixed with 250 mL of lukewarm water. This mixture was left at room temperature (20°C) for 20 min. In a separate bowl approximately 50 mL of olive oil, 5 g of salt and 750 g of plain flour were dry blended. The yeast mixture was added to the flour and the mix was kneaded lightly. The dough was then covered and allowed to rest for 2 h or until it doubled in volume. The dough was kneaded on a floured board and rolled out into a base 1 cm thick and approximately 40 cm x 25 cm (length x width). The pizza dough was baked in an oven at 200°C for 15 min, cooled to ambient temperature and stored pending use in sensory assessment panels.

CHAPTER 4

Thermal inactivation of enzymes during tomato processing

Enzymes are an integral part of all plants and are responsible for a range of desirable and undesirable reactions (Pilnik and Voragen, 1991; Snir *et al.*, 1996). For example, enzymes such as peroxidase can aid development of ripening and senescence in fruits; however, post-harvest it can cause development of off-flavours and odours. Similarly, pectolytic enzymes such as pectinmethylesterase and polygalacturonase are beneficial in textural changes during the ripening process but during storage or processing can cause undesirable changes such as loss of cloud instability, decrease in juice viscosity and decrease in juice yield. Sometimes enzymes can be deliberately added or used to bring about desirable reactions or changes such as the extraction of juice from cellulose components during the clarification of fruit juices to produce sparkling juices (Mans, 1992). The enzymes most commonly of concern in tomato processing are peroxidase (PO, EC1.11.1.7), pectinmethylesterase (PME, EC3.1.1.11) and polygalacturonase (PG, EC3.2.1.15).

4.1. Thermal inactivation of PO, PME and PG enzymes in fresh tomatoes

4.1.1. Introduction

Tomato enzymes are usually thermally inactivated in commercial practice at temperatures in excess of 90°C for a period of up to 20 minutes. Although heat-inactivation of enzymes is still the most common method of deteriorative enzyme inactivation, other non thermal strategies such as microwave energy (Ramaswamy and Fakhouri, 1998), high pressure (Cano *et al.*, 1997; Donsi *et al.*, 1996; Hernandez and Cano, 1998) and supercritical carbon dioxide (Arreola *et al.*, 1991) are less detrimental to sensitive flavour and aroma components and have also been investigated. Some researchers have also investigated the use of lower enzyme inactivation temperatures so that heat sensitive flavour and aroma components can be preserved during processing (Porretta, 1991).

The aim of this study was to investigate the heat stability characteristics of the main deteriorative enzymes in processing varieties of tomatoes to more closely define the minimum time/temperature regimes required for effective inactivation of these enzymes. Thermal inactivation of PO, PME and PG enzymes during tomato processing is necessary to avoid undesirable deteriorative reactions which lead to the loss of cloud stability and decrease of juice yield and juice viscosity. Due to the limited availability of fresh processing varieties throughout the year, this research also involved investigation of these enzymes in stored samples of both blanched and frozen processing tomato varieties and this work is described in Section 4.2.

4.1.2. Materials and methods

Two processing varieties of Roma tomatoes, UC82B and Alta, were obtained from Unifoods (Tatura, Victoria). The UC82B variety was tested over two processing seasons, however the Alta variety was only tested for the first season. The fruits were obtained in February during the early part of the harvest. The harvesting index was a pH value of below 4.4. Tomatoes were sorted and washed, then both immediately chilled and held at 4°C or frozen below -18°C. Tomatoes were blended and the tomato pulp and juice were thermally treated as described in Section 3.2. The UC82B variety was processed at two break temperatures viz. 85°C and 95°C whereas the Alta was only inactivated at 95°C. Commercially processed juices prepared at two break temperatures of 85°C and 95°C were also obtained from Berrivale Ltd. (Berrivale, South Australia). The colour, pH, soluble solids and titratable acidity of the tomato juices were analysed according to the methods described in Sections 3.3.1.1, 3.3.2.3, 3.3.2.4 and 3.3.2.7 respectively. Enzyme extracts from the thermally treated pulp samples were prepared according to Section 3.2.1.1. These extracts were analysed for PO, PME and PG enzyme activity using the methods described in Sections 3.2.1.2, 3.2.1.3 and 3.2.1.4 respectively. The thermal process inactivation times for PO, PME and PG were determined using the method described in Section 3.2.2.

4.1.3. Results and discussion

The analyses done on UC82B and Alta tomatoes are summarised in Table 4.1 and represent the average of 3 replicates. The results show that, during the same season (season 1), tomatoes of the Alta variety had higher pH and lower titratable acidity than tomatoes of the UC82B variety ($P \leq 0.05$). The Alta variety also generally had higher soluble solids and total solids content than tomatoes of the UC82B variety ($P \leq 0.05$). Similarly the deteriorative PO and PME enzyme activities were higher in the Alta variety than in the UC82B variety ($P \leq 0.05$), while the PG enzyme activity of both varieties was not significantly different.

Seasonal variation, studied in UC82B tomatoes, showed that the tomatoes from season 1 had lower pH and higher titratable acidity than season 2 tomatoes ($P \leq 0.05$). The tomatoes from season 1 also had higher soluble solids and total solids content than tomatoes from season 2 ($P \leq 0.05$). These variations may be due to the lower rainfall experienced in season 1 than in season 2 during the fruit development and maturation stages. Lower rainfall and the resulting high water stress during fruit development and ripening stages can produce crops with higher fruit constituents due to the increase in cell osmolarity (Stevens, 1985). In the UC82B variety, the PO, PME and PG enzyme activities were higher ($P \leq 0.05$) during the higher rainfall season. This may be due to the higher moisture availability for the enzymatic reactions. Generally at low moisture levels the enzymatic reaction is affected negatively due to the lower diffusion rate of the enzyme (Reed, 1975).

In the UC82B variety the juices obtained using the two different break temperatures had slightly different compositions (Table 4.2). The juice obtained from the higher break temperature (95°C) had higher total solids, soluble solids and suspended solids contents than that obtained from the lower break temperature ($P \leq 0.05$). This is due to more pectins and other cellulosic material being extracted from the juice at higher break temperatures (Luh and Daoud, 1971).

Table 4.1 Analyses of fresh tomato pulp from UC82B and Alta varieties

Parameter	Alta	UC82B	
	Season 1	Season 1	Season 2
pH	3.95 - 4.40	3.89 - 4.12	4.56 - 4.68
Acidity (g/100g citric acid)	0.23 - 0.32	0.35 - 0.38	0.23 - 0.31
Soluble solids (°Brix)	5.00 - 5.55	5.15 - 5.25	4.60 - 4.95
Total solids (% w/w)	5.75 - 7.00	5.74 - 6.55	5.50 - 5.65
Colour (L*a*b*)	42.65, +18.02, +20.88	43.12, +19.1, +20.22	N/A
PO enzyme activity (Δabs/min/mL)	2.97	2.01	2.55
PME enzyme activity (μmoL/min/mL)	10.73	8.53	10.75
PG enzyme activity (nmol/min/mL)	9.59	9.73	11.35

Standard errors: pH ± 0.25; acidity ± 0.12; soluble solids ± 0.95; total solids ± 0.82; PO ± 0.30; PME ± 0.50; PG ± 0.92

Table 4.2 Composition of tomato juice obtained from the UC82B variety using break temperatures of 85°C and 95°C

Sample	Total Solids (% w/w)	Soluble Solids (°Brix)	Suspended Solids (% w/w)	Viscosity (mPa.s)
Juice 85°C break	5.49	4.80	1.42	590
Juice 95°C break	5.57	4.90	1.48	620

Standard errors: total solids ± 0.69; soluble solids ± 0.85; suspended solids ± 0.52; viscosity ± 10.20

Figures 4.1 - 4.6 show the thermal resistance and thermal inactivation graphs for PO, PME and PG enzymes in both varieties. The data used to plot the graph is the mean of three replicates. The D and z values were calculated from the thermal resistance time graphs (TRT) and are reported in Table 4.3.

The D-value is the time in minutes required to reduce the enzyme activity by 90% at any given temperature, i.e., to cause a 10-fold reduction in enzyme activity. The z-value is the number of degrees Celsius required to reduce the D-value by one log cycle i.e. the difference in temperature required for the thermal resistance graph to complete one cycle. The D-value is inadequate to fully describe the thermal process because it only reports the time required for a 10-fold reduction of enzyme activity. During tomato processing, complete inactivation of enzymes is

necessary to ensure optimum product quality, which is why the F-values have been calculated.

The F-value is defined as the time in minutes required for the complete inactivation of all the enzyme and can be calculated from the thermal inactivation time plots (TIT). The drawback with using F-values alone is that they are based on the initial enzyme concentration, which may vary from batch to batch. For this reason it is important that both D and F values are utilized during thermal process calculations. Figures 4.1 and 4.2 show that PO can be very easily inactivated at temperatures below 70°C, which is markedly lower than the break temperatures currently used during commercial tomato processing. The pectolytic enzymes PME and PG in the tomato varieties studied appeared to be more heat resistant than the PO enzyme and therefore required higher inactivation temperatures as shown in Figures 4.3, 4.4, 4.5 and 4.6.

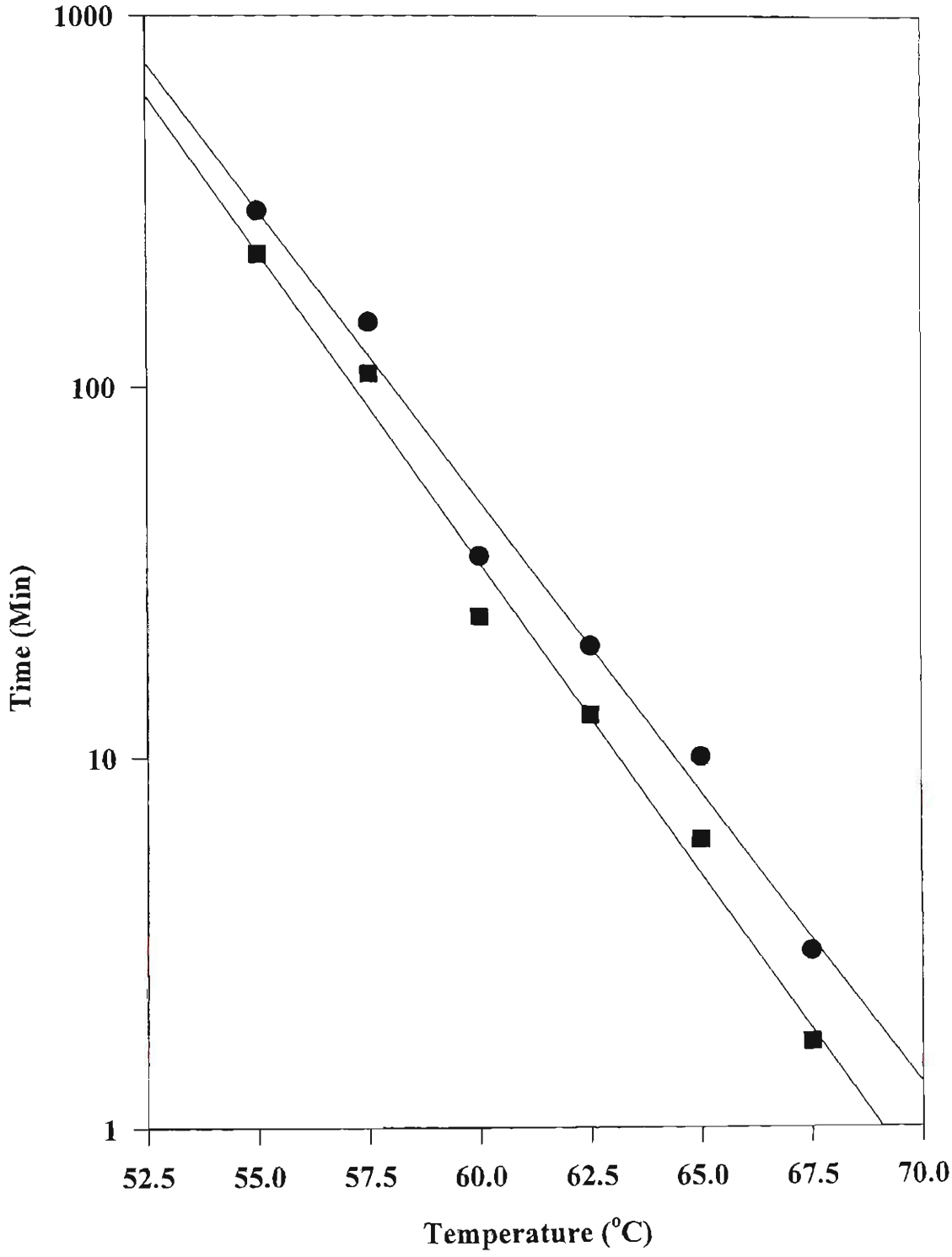


Figure 4.1 Thermal resistance (■) and thermal inactivation (●) of PO enzyme in UC82B tomatoes

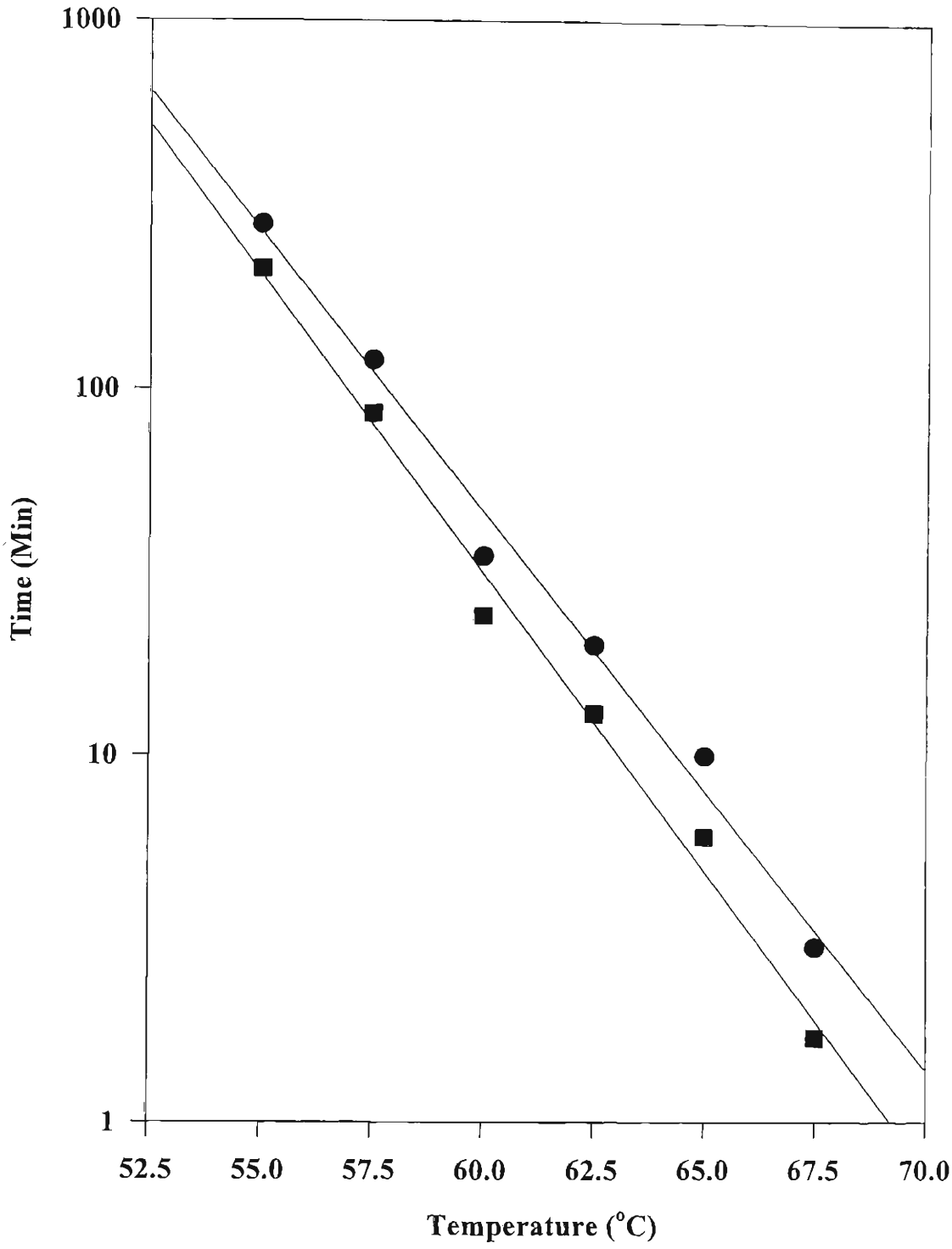


Figure 4.2 Thermal resistance (■) and thermal inactivation (●) of PO enzyme in Alta tomatoes

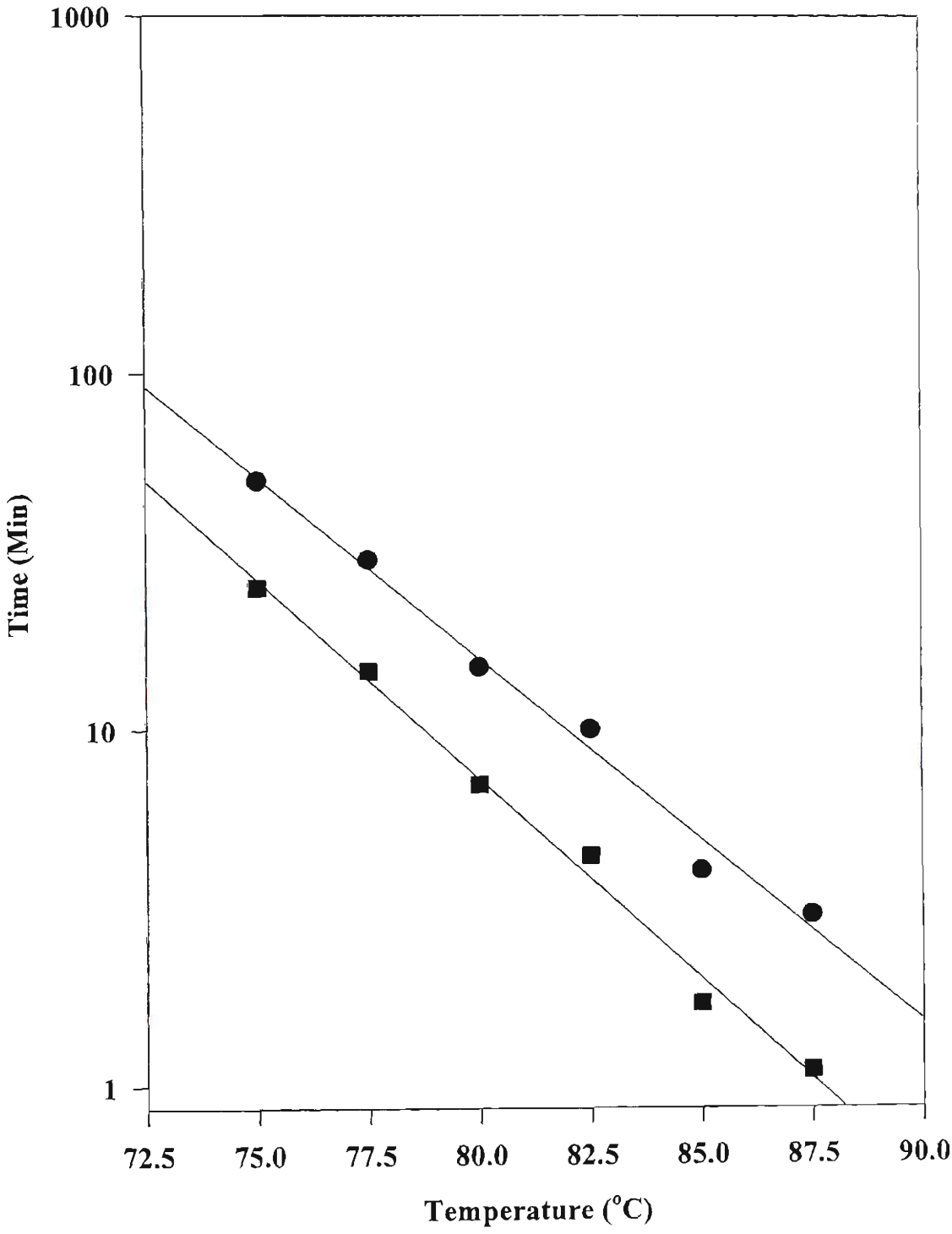


Figure 4.3 Thermal resistance (■) and thermal inactivation (●) of PME enzyme in UC82B tomatoes

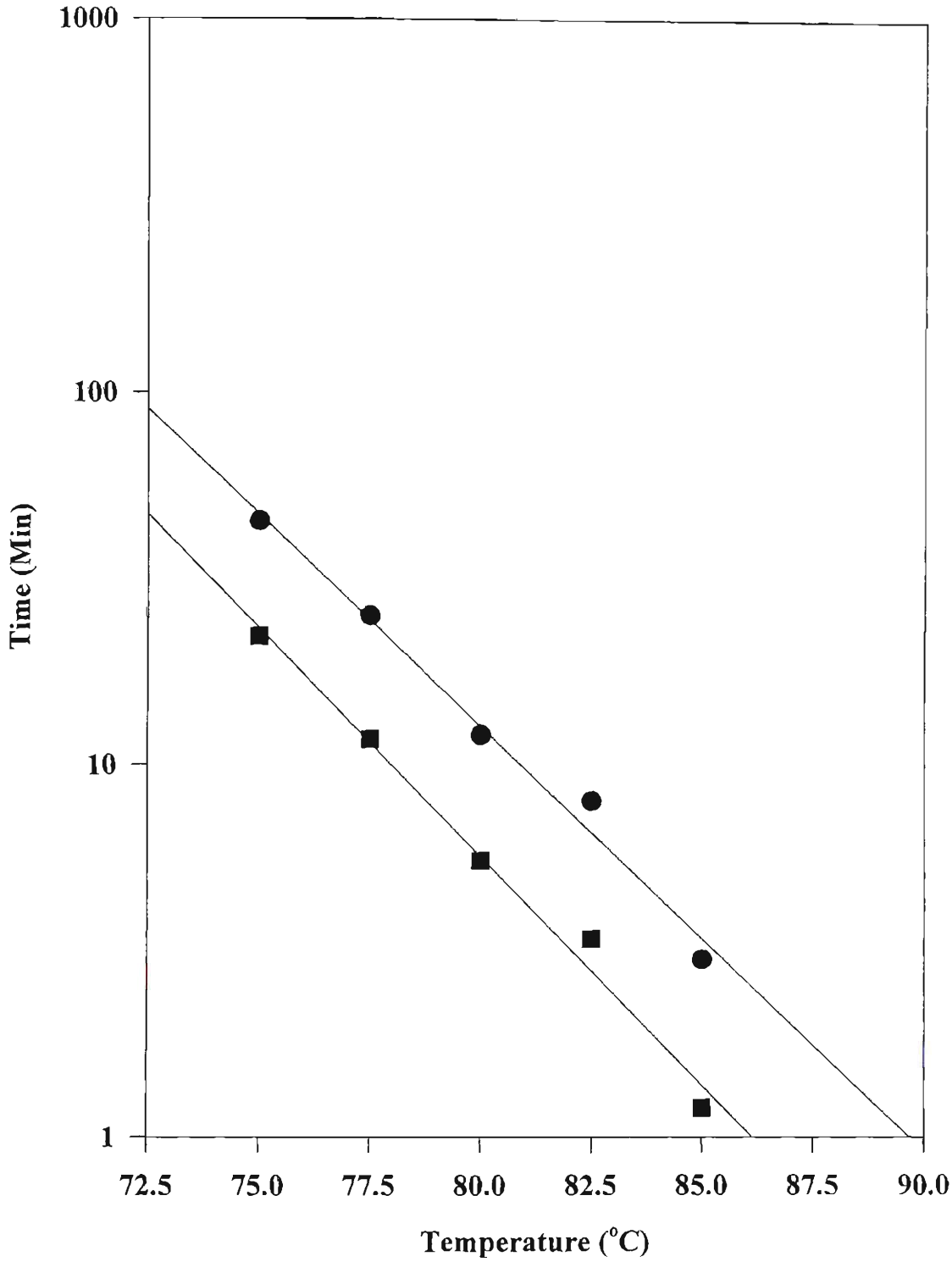


Figure 4.4 Thermal resistance (■) and thermal inactivation (●) of PME enzyme in Alta tomatoes

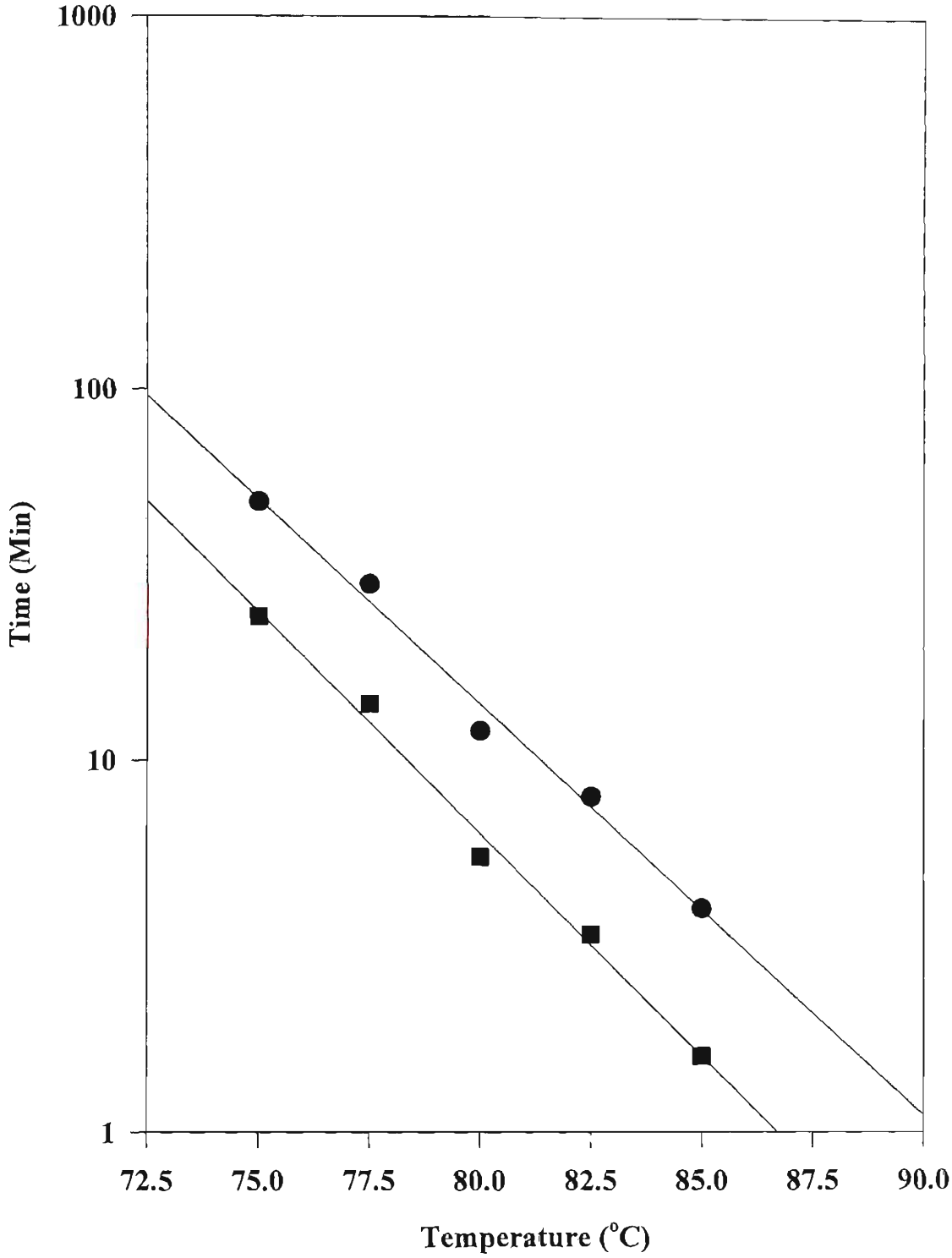


Figure 4.5 Thermal resistance (■) and thermal inactivation (●) of PG enzyme in UC82B tomatoes

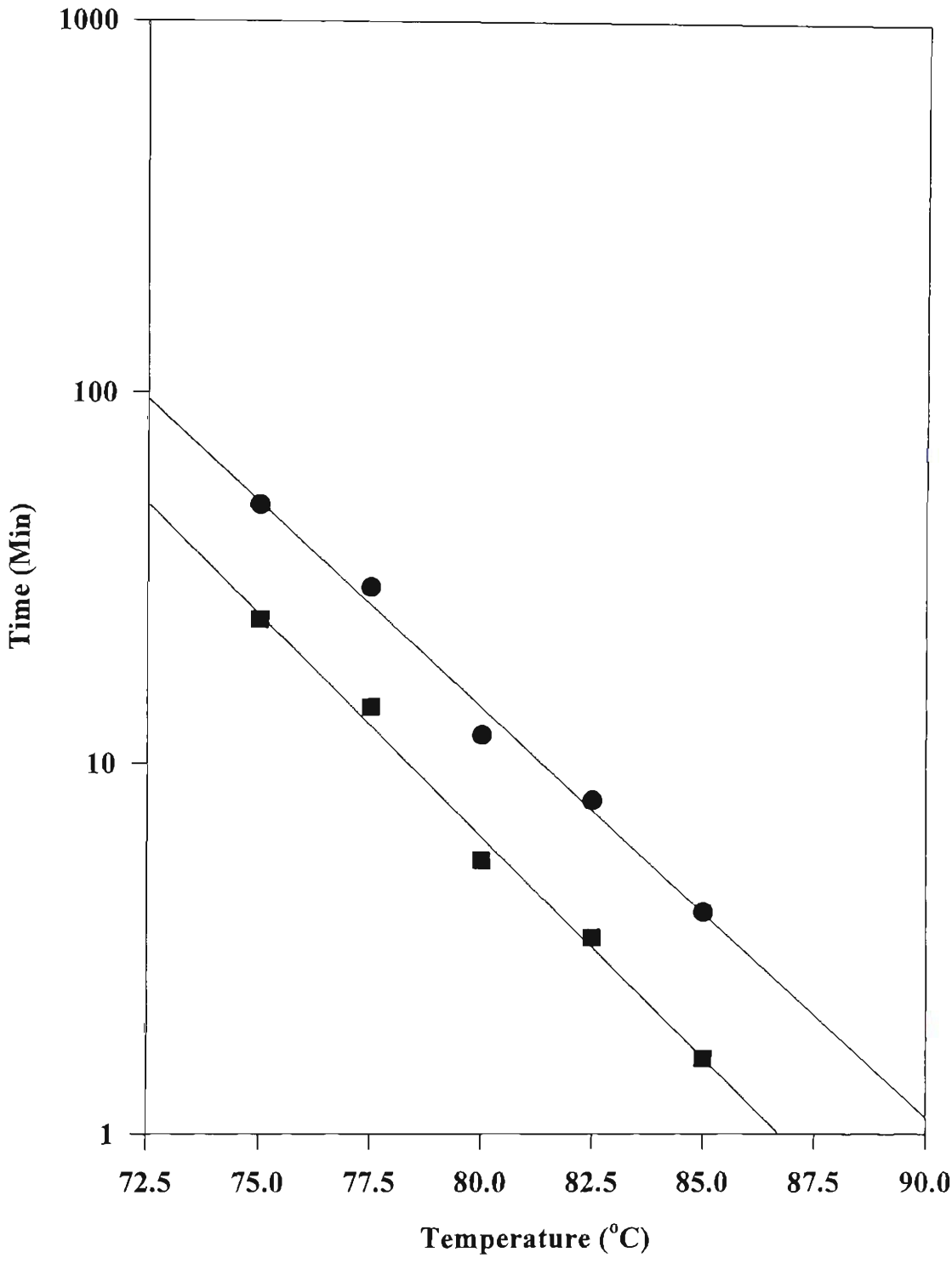


Figure 4.6 Thermal resistance (■) and thermal inactivation (●) of PG enzyme in Alta tomatoes

As the data in Table 4.3 indicate, the PME and PG enzymes in both of the varieties studied had higher D-values than the PO enzyme ($P \leq 0.05$). The most heat resistant enzyme studied was PME from the UC82B variety while the PG enzymes in both of the varieties exhibited the same heat stability. The PO enzyme, which is frequently used as an indicator enzyme for assessing blanching effectiveness, from both of the varieties studied was inactivated at considerably lower temperatures than both PME and PG and therefore is not suitable for assessing the effectiveness of the heat process required to fully inactivate the deteriorative enzymes in tomato processing. Indeed it is proposed that for tomatoes, PME would be the more appropriate enzyme for assessing adequacy of heat treatment.

Studies of the PME enzyme from Italian varieties of tomatoes of comparable pH showed higher F/D ratios (in the range 5.3 to 6.1) than those found in the Australian varieties of tomatoes used in this study (Larrata *et al.*, 1995). This suggests that the PME enzymes from the Australian processing varieties may be less heat stable than those from the Italian varieties. This difference in heat stability may also enable Australian tomato processors to prepare better quality end products since the deteriorative enzymes can be inactivated at lower temperatures. Other studies on the PME enzymes from Indian Pusa-Ruby tomatoes reported z-values similar to those reported in this study except at lower inactivation temperatures (Nath *et al.*, 1983). Therefore the PME enzymes from the Australian varieties studied may be more heat stable than the Indian variety of Pusa-Ruby tomatoes. These differences in the F/D ratios may be due to geographical differences that offer different growth conditions, as well as genetic differences and may require further investigation.

Thermal inactivation studies are based on the enzyme concentration in a particular batch of tomatoes. Often however, the initial enzyme concentration in subsequent batches may be higher than that in the test batch and therefore, for any given processing temperature, a higher D-process may be required to allow a safety margin during processing. The recommended D-process would thus require a

slightly longer processing time and typically a 25% safety margin is allowed in commercial situations. Table 4.4 shows the proposed recommended D-processes incorporating the 25% safety margin and the corresponding process times for PG, PME and PO enzyme inactivation in the varieties used in this study.

Table 4.3 Summary of D, F and z values for PO, PG and PME enzymes in Alta and UC82B tomatoes

Enzyme	Variety	D value (min) from TRT curve	F value (min) from TIT curve	F/D
PO	UC82B	6.0 D = 0.70 70.0°C	6.2 F = 1.50 70.0°C	2.14
	Alta	6.2 D = 0.75 70.0°C	6.5 F = 1.50 70.0°C	2.00
PME	UC82B	9.0 D = 1.00 87.5°C	9.7 F = 2.80 87.5°C	2.80
	Alta	8.2 D = 1.00 87.5°C	8.7 F = 2.65 87.5°C	2.65
PG	UC82B	8.1 D = 0.80 87.5°C	8.6 F = 2.20 87.5°C	2.75
	Alta	8.1 D = 0.80 87.5°C	8.6 F = 2.20 87.5°C	2.75

Standard errors: D value ± 0.55; F value ± 0.78; F/D ± 0.48

Table 4.4 Process schedule recommended for commercial processing of UC82B and Alta tomatoes

Enzyme	Variety	F/D	Recommended F/D	Calculated process time for recommended D-process (min)
PO	UC82B	2.14	2.7	1.89
	Alta	2.00	2.5	1.88
PME	UC82B	2.80	3.5	3.50
	Alta	2.65	3.3	3.30
PG	UC82B	2.75	3.4	2.56
	Alta	2.75	3.4	2.56

4.2. Thermal inactivation of PO, PME and PG enzymes in blanched tomatoes and frozen tomatoes

4.2.1. Introduction

Blanching is the initial heat treatment used for the purpose of stabilizing enzyme and microbial activities. The blanching process is usually a prerequisite for subsequent processing operations such as freezing or dehydration. Advantages of blanching include the expulsion of dissolved air from plant tissue, shortening of cooking time inactivation of deteriorative enzymes and reduction of microbial load (Poulsen, 1986). Traditionally blanching involves the immersion of the product in hot water for a defined period but modern blanching methods use much more sophisticated approaches and equipment such as microwave blanching (Hill, 1987).

The freezing process is generally used in addition to the blanching process and is one of the most common methods of food preservation. The freezing process generally suspends microbial growth and enzyme activity. There are two types of freezing methods applied in the food industry, slow and fast. Slow freezing results in larger ice crystals hence inferior quality. However, if the vegetables are stored for longer periods the difference in quality between fast and slow frozen vegetables decreases markedly (Charoenrein and Reid, 1989). The final quality of frozen vegetables is dependent on two factors, the storage time and the storage temperature. Blanching vegetables prior to freezing has many advantages as mentioned earlier, however there are also some disadvantages that can arise from the combination of these two processes. For example, blanched frozen vegetables exhibit some loss in texture, cooked taste and deterioration of flavour (Williams *et al.*, 1986).

In Australia, processing tomatoes are only available for a few months of the year and most of the thermal enzyme inactivation studies could not be completed within this time frame. Suitable freezing and blanching processes were investigated to preserve the test batch of tomatoes for subsequent enzyme studies. For the purpose of this work, the freezing and blanching processes were

performed as independent processes. Both frozen and blanched frozen tomatoes were thermally treated and residual PO, PME and PG enzyme activities were measured.

4.2.2. Materials and methods

UC82B and Alta varieties of tomatoes were sorted and washed then either thermally treated for enzyme studies, or frozen below -18°C for approximately 30 days before commencing thermal inactivation studies, or blanched in water for 3 minutes at 97°C then immediately thermally treated without storage (Section 3.1.2). Tomato pulp was prepared and thermally treated using the method described in Section 3.2. The enzyme extract was prepared from the thermally treated samples as described in Section 3.2.1.1 and analysed for PO, PME and PG enzymes as described in Sections 3.2.1.2, 3.2.1.3 and 3.2.1.4 respectively.

4.2.3. Results and discussion

As expected, the residual PO enzyme activity was higher ($P \leq 0.05$) in fresh tomatoes than in either frozen or blanched tomatoes in both of the varieties studied (Figure 4.7). The initial PO enzyme activity of fresh tomatoes was higher in the Alta variety than in the UC82B variety ($P \leq 0.05$). Similarly the frozen and blanched Alta tomatoes had higher initial PO enzyme activity than the frozen UC82B tomatoes ($P \leq 0.05$). Despite the higher initial PO enzyme activity in fresh, frozen and blanched Alta tomatoes, the PO enzyme from the UC82B variety was more heat stable and took longer to inactivate therefore requiring a longer D-process (Table 4.4). The freezing process reduced the enzyme activity by 38% in the UC82B variety and by 53% in the Alta variety, however the residual enzyme in frozen tomatoes appeared to be more heat stable and therefore more difficult to inactivate. In both of the tomato varieties studied, the blanching process reduced the PO enzyme activity by 80% of the initial enzyme activity of fresh tomatoes ($P \leq 0.05$). Since the residual PO enzyme activities of the blanched tomatoes were considerably lower than in the fresh tomatoes ($P \leq 0.05$), a quick pre-blanching process may enable a reduction in the overall thermal break processing conditions

thus lessening the degradation of heat sensitive flavour or colour components of tomatoes.

The residual PME enzyme activities showed similar trends as that noted for the PO enzyme. As indicated by Figures 4.8 and 4.9, blanched tomatoes had significantly lower PME activities than fresh or frozen tomatoes for both of the varieties studied ($P \leq 0.05$). The tomatoes of the Alta variety had higher initial PME enzyme activity than the UC82B tomatoes (approximately 10.7 vs 8.5 μmole/min/mL), however the PME enzyme from the UC82B variety was more heat stable and required a higher D-process than the Alta variety (Tables 4.3 and 4.4). The freezing process reduced the enzyme activity in the UC82B variety by about 2% whereas in the Alta variety a higher inactivation level of 18% was achieved. As compared to the reduction of PO enzyme activity, freezing only marginally affected the PME enzyme activity. The PME of frozen tomatoes showed similar trends in heat stability to the PO enzyme of frozen tomatoes and appeared to be more heat stable than that of fresh or blanched tomatoes for both of the varieties studied. The PME of frozen UC82B tomatoes was more difficult to inactivate than the PME of frozen Alta tomatoes. The blanching process reduced PME activity by 75% ($P \leq 0.05$) in both of the varieties studied and thus potentially could be used as a pre-treatment to reduce the intensity of the thermal break process, so allowing valuable components to be retained.

The initial PG enzyme activities of both varieties were very similar but showed a different trend to that experienced with the PO and PME activities. The frozen UC82B and Alta tomatoes had higher ($P \leq 0.05$) residual PG enzyme activities (approximately 7-8%) than in fresh tomatoes (Figures 4.10 and 4.11). The higher level of PG activity in frozen tomatoes is somewhat unexpected and may require further investigation since this result is not in agreement with that noted by Marangoni *et al.* (1995) where chilled tomatoes showed no significant differences in PG activity. Generally the PG enzyme from frozen tomatoes was more difficult to inactivate than from the fresh or blanched tomatoes in both of the varieties studied. The blanching process was quite effective in reducing the enzyme

activity to 55% of the initial value in both of the varieties studied ($P \leq 0.05$). Although according to Figures 4.10 and 4.11 it appeared that the PG enzyme from the Alta variety was slightly more heat stable, the PG enzyme from both of the varieties had the same heat stability and required the same D process for thermal inactivation (Table 4.4).

In summary, the PO enzyme from both of the varieties showed less heat stability than PME and PG enzymes. The PO enzyme from the UC82B variety was slightly more heat stable than the Alta variety. Similarly the PME enzyme from the UC82B variety was more heat stable than that from the Alta variety. In both of the varieties studied PG enzyme had the same heat stability. The freezing process seemed to reduce PO enzyme activity significantly, however PME activity was only reduced marginally in the case of both of the varieties studied. The PG enzyme activity appeared to be slightly enhanced by the freezing process. According to the findings of this study, blanching significantly reduced the activities of all of the three enzymes studied in both of the varieties hence it could be used as an initial pre-break process to minimise the intensity of the thermal break process itself.

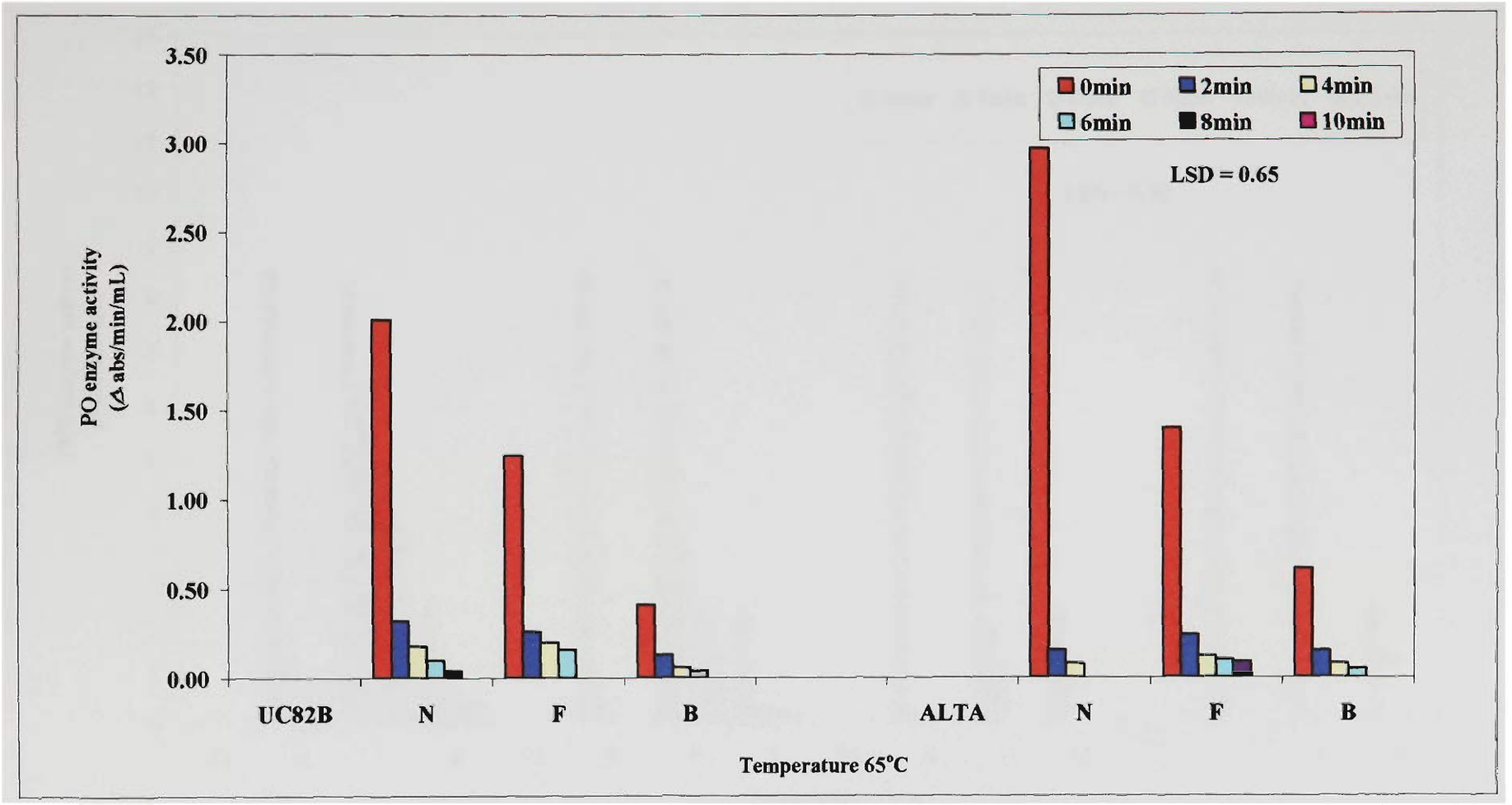


Figure 4.7 **Residual PO enzyme activity in fresh (N), frozen (F) and blanched (B) UC82B and Alta tomatoes following heat treatment at 65°C for various periods of time**

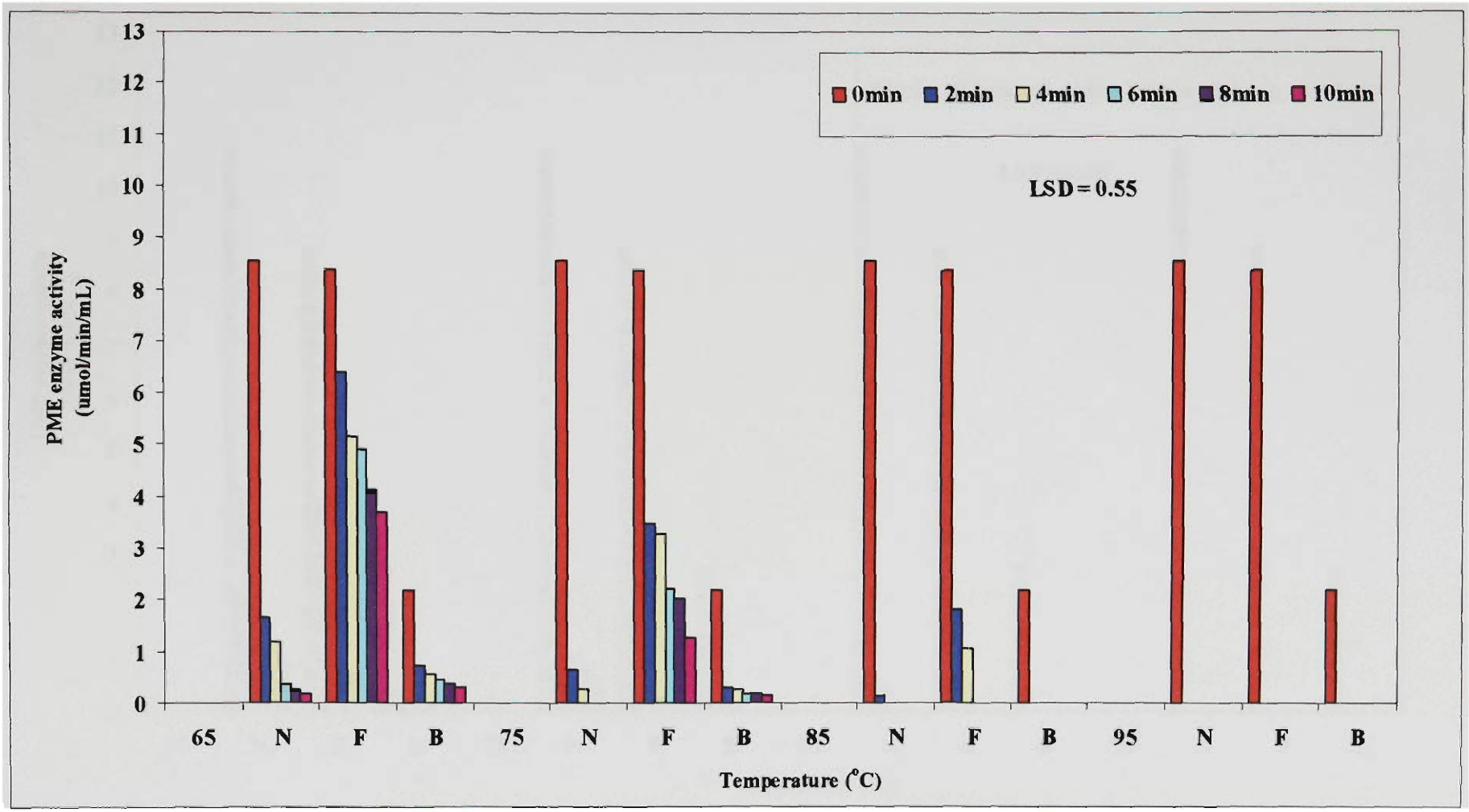


Figure 4.8 **Residual PME enzyme activity in fresh (N), frozen (F) and blanched (B) UC82B tomatoes following heat treatment at different temperatures for various periods of time**

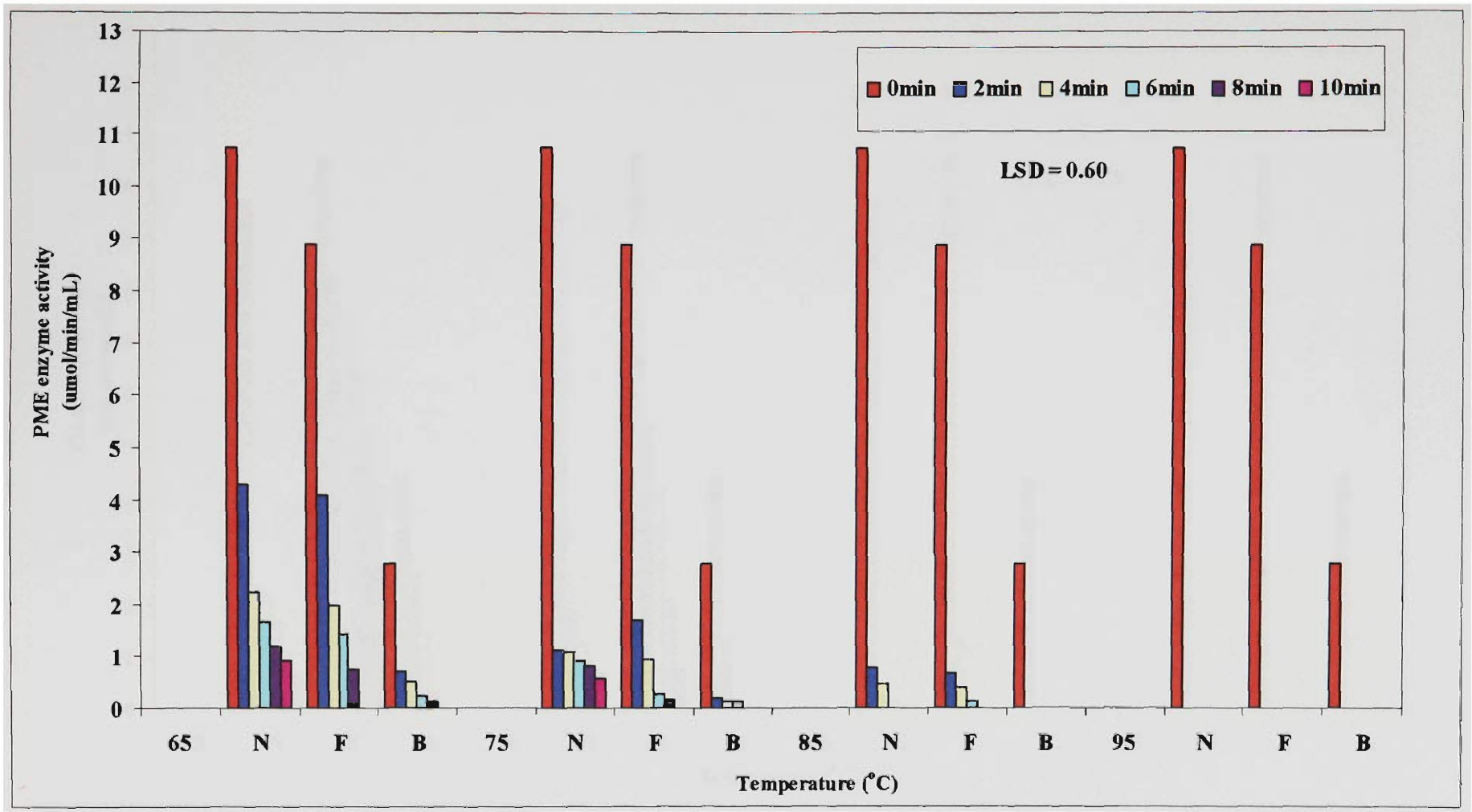


Figure 4.9 **Residual PME enzyme activity in fresh (N), frozen (F) and blanched (B) Alta tomatoes following heat treatment at different temperatures for various periods of time**

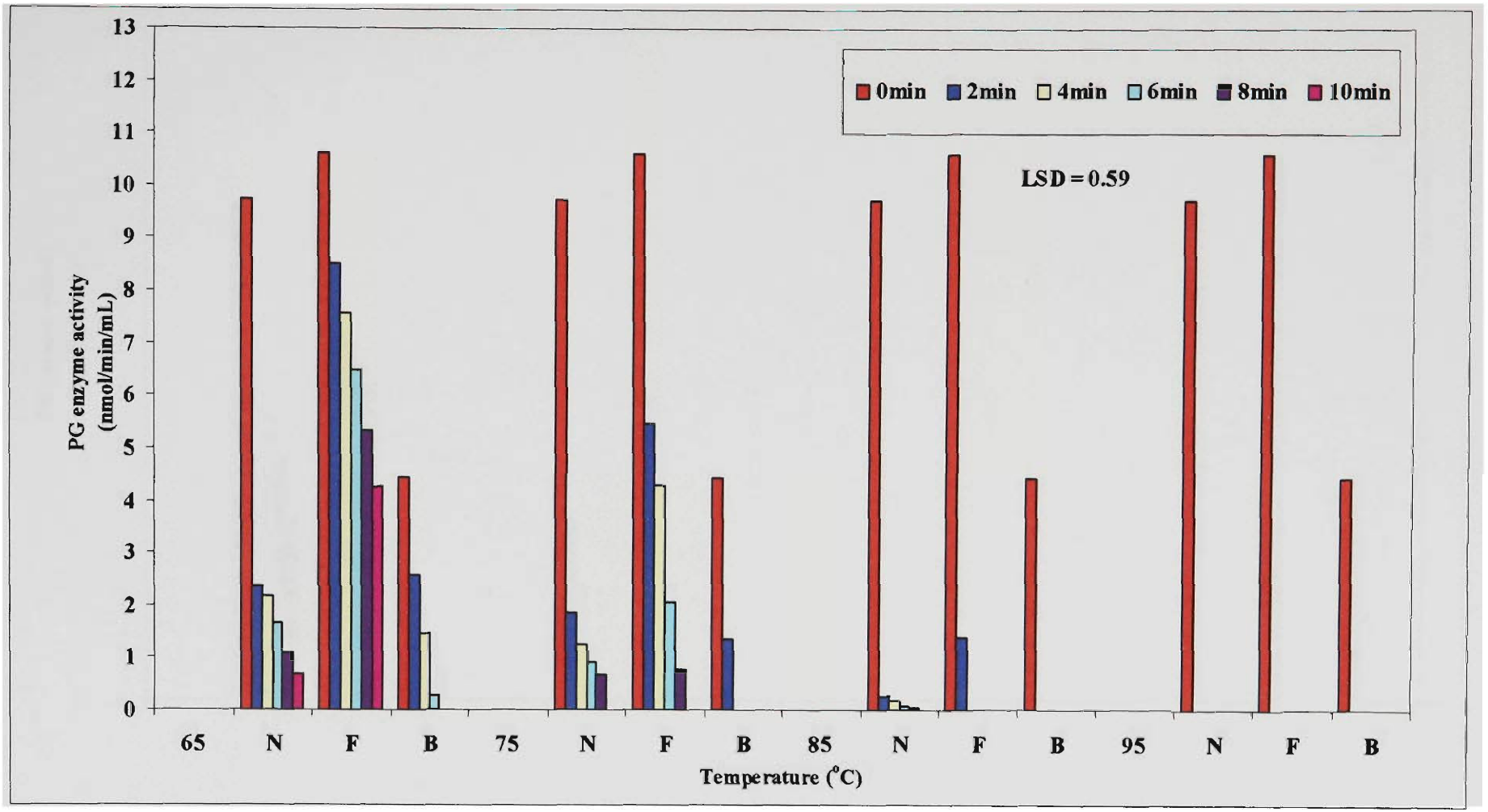


Figure 4.10 **Residual PG enzyme activity in fresh (N), frozen (F) and blanched (B) UC82B tomatoes following heat treatment at different temperatures for various periods of time**

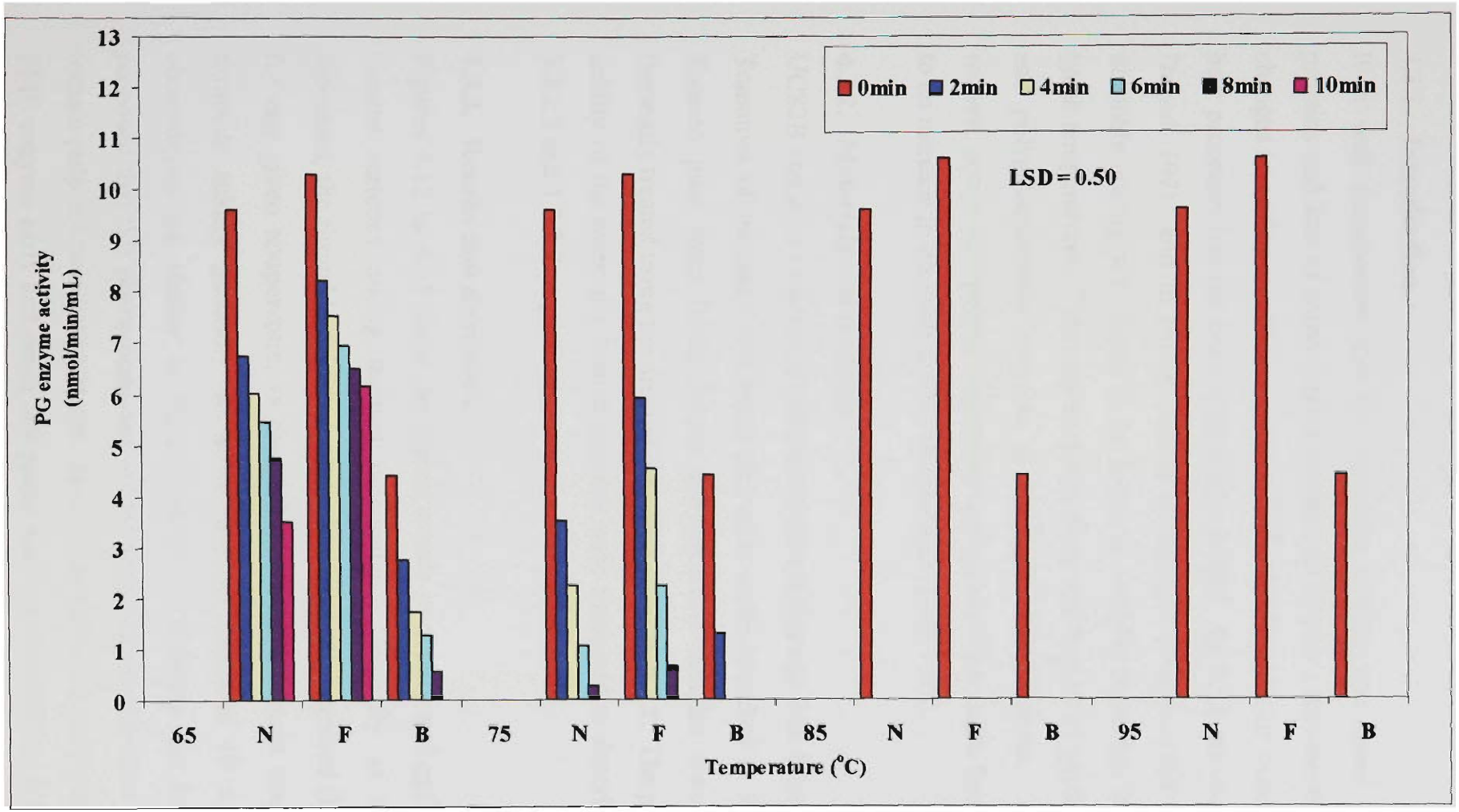


Figure 4.11 **Residual PG enzyme activity in fresh (N), frozen (F) and blanched (B) Alta tomatoes following heat treatment at different temperatures for various periods of time**

4.3. The effect of thermal treatment on pH and titratable acidity of fresh, frozen and blanched tomatoes

4.3.1. Introduction

It is well documented that the blanching process can cause denaturation of proteins and loss of some volatile aroma and flavour components. However the changes in acidity levels of vegetables immediately after the blanching or similar heat processes has not been extensively studied. In fresh tomato pulp (Luh and Daoud, 1971) and in frozen tomato concentrate (Fonseca and Luh, 1976) the titratable acidity was found to be lower in samples that were heated at higher break temperatures. This may be due to rapid inactivation of pectinmethylesterase and polygalacturonase enzymes at the higher temperatures. These enzymes convert pectin into pectic, oligouronic and galacturonic acids hence contributing to an increase in titratable acidity (Fonseca and Luh, 1976).

4.3.2. Materials and methods

UC82B and Alta varieties of tomatoes were washed and then frozen below -18°C. Tomatoes of the same test batch also were water blanched at 97°C for 3 min. Tomato pulp from fresh, frozen and blanched samples were prepared and thermally treated using the method described in Section 3.2. The pH and titratable acidity of the thermally treated samples were measured as described in Sections 3.3.2.3 and 3.3.2.7 respectively.

4.3.3. Results and discussion

Figures 4.12 to 4.15 show the typical trends in acidity and pH changes in the tomato varieties during thermal processing. Generally as the temperature increased, the titratable acidity decreased and the pH increased ($P \leq 0.05$). Also for any given temperature, as the period of heat treatment was increased, the titratable acidity generally decreased and pH increased ($P \leq 0.05$). These observations are similar to those reported by Fonseca and Luh (1976) who proposed that this phenomena was related to the de-esterification of pectin in the tomato pulp at lower temperatures. Heating at higher temperatures inactivated the PME enzyme early and hence the pectin was not converted to pectic, oligouronic

or galacturonic acids (Fonseca and Luh, 1976). This phenomenon may also explain the lower titratable acidity levels of blanched tomatoes in both of the varieties studied. Although a pre-blanching process can be used to reduce the duration of the thermal break process, a slight reduction of acidity may occur in the final tomato concentrate and may need to be compensated for by the addition of citric acid to the final product.

Frozen tomatoes of both the varieties studied had higher titratable acidity than the fresh tomatoes ($P \leq 0.05$) and this could be explained by the increased difficulty in inactivating PO, PME and PG from frozen tomatoes, which was reported earlier in Section 4.2.3. However, the difference in the titratable acidity between frozen and fresh tomatoes of both varieties diminished with severity of the heat treatment. Such observations would be expected in keeping with the proposal of Fonseca and Luh (1976) and supported by the enzyme inactivation studies reported earlier in Section 4.1, given that the greater the severity of the heat treatment the more rapid and extensive the inactivation of PME and hence the less the extent of pectic and other acid production. Similar observations regarding titratable acidity were observed for blanched tomatoes of both varieties. Cano (1995) also suggested that the higher titratable acidity and lower pH levels in frozen vegetables might be due to the concentration of organic and inorganic salts in the aqueous phase of the plant tissue.

The overall differences in titratable acidity between the two fresh varieties were reported earlier in Table 4.1, which showed that, within the same growing season, the UC82B variety had higher titratable acidity and lower resultant pH than the Alta variety ($P \leq 0.05$).

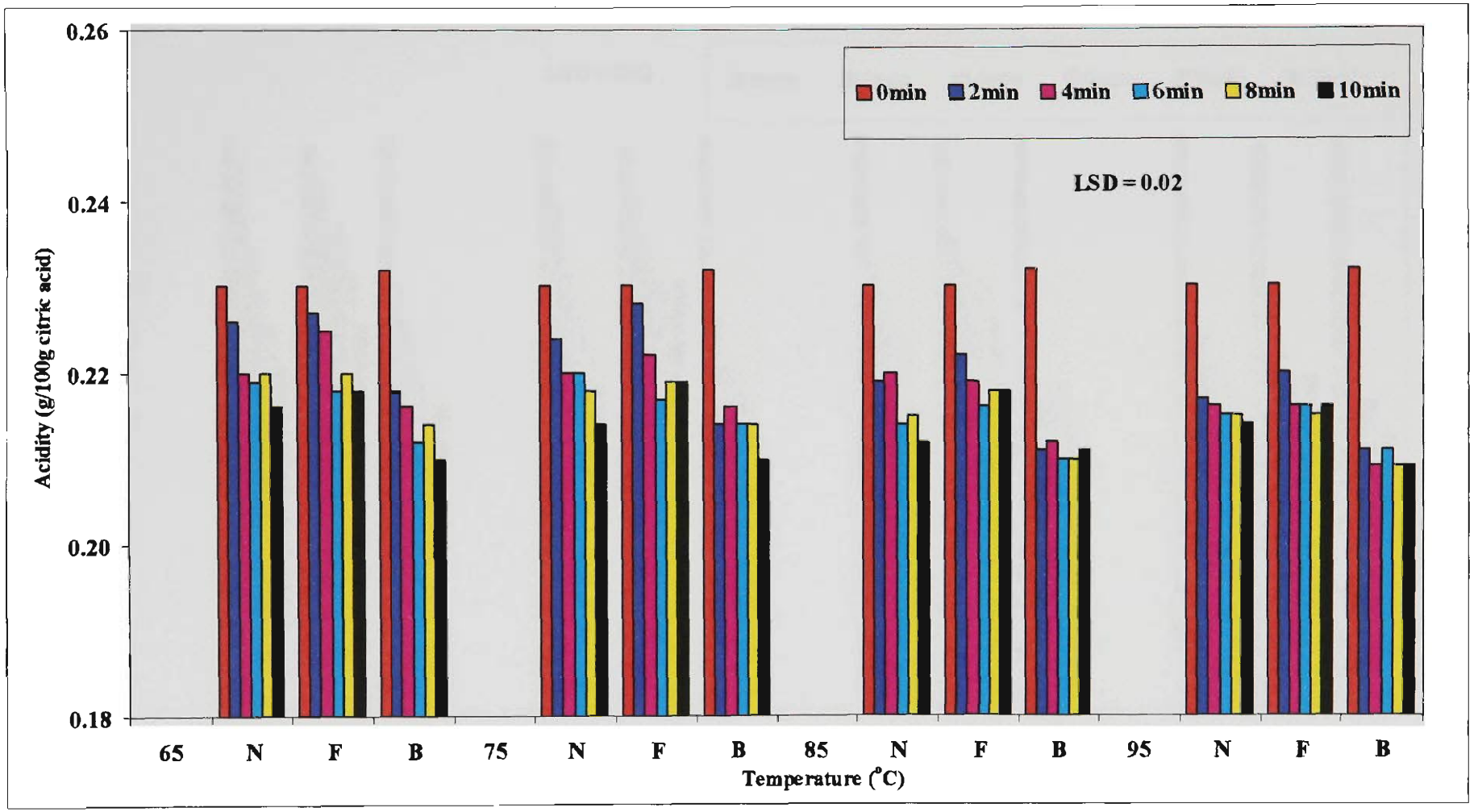


Figure 4.12 Acidity of thermally treated pulp prepared from fresh (N), frozen (F) and blanched (B) UC82B tomatoes

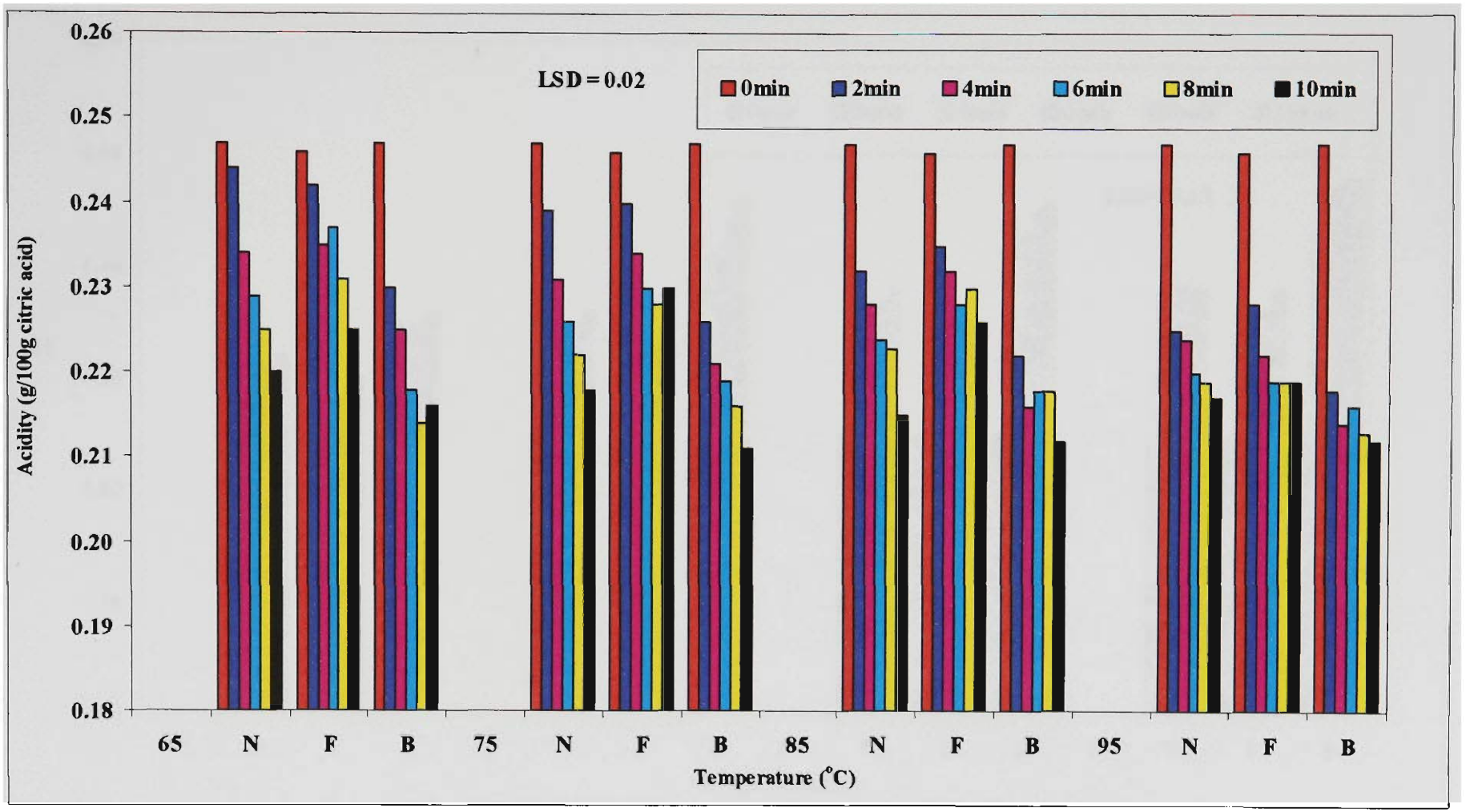


Figure 4.13 Acidity of thermally treated pulp prepared from fresh (N), frozen (F) and blanched (B) Alta tomatoes

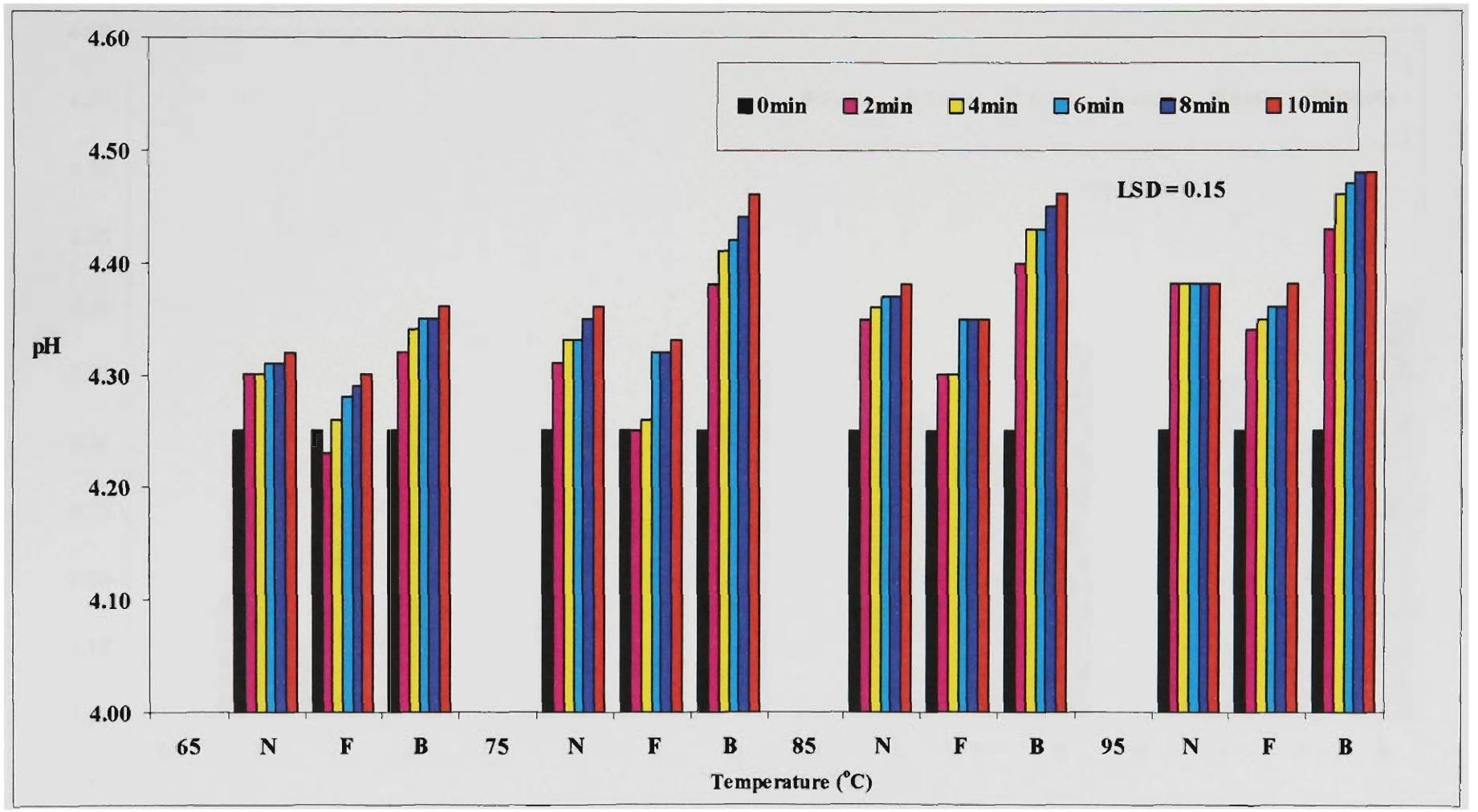


Figure 4.14 pH of thermally treated pulp prepared from fresh (N), frozen (F) and blanched (B) UC82B tomatoes

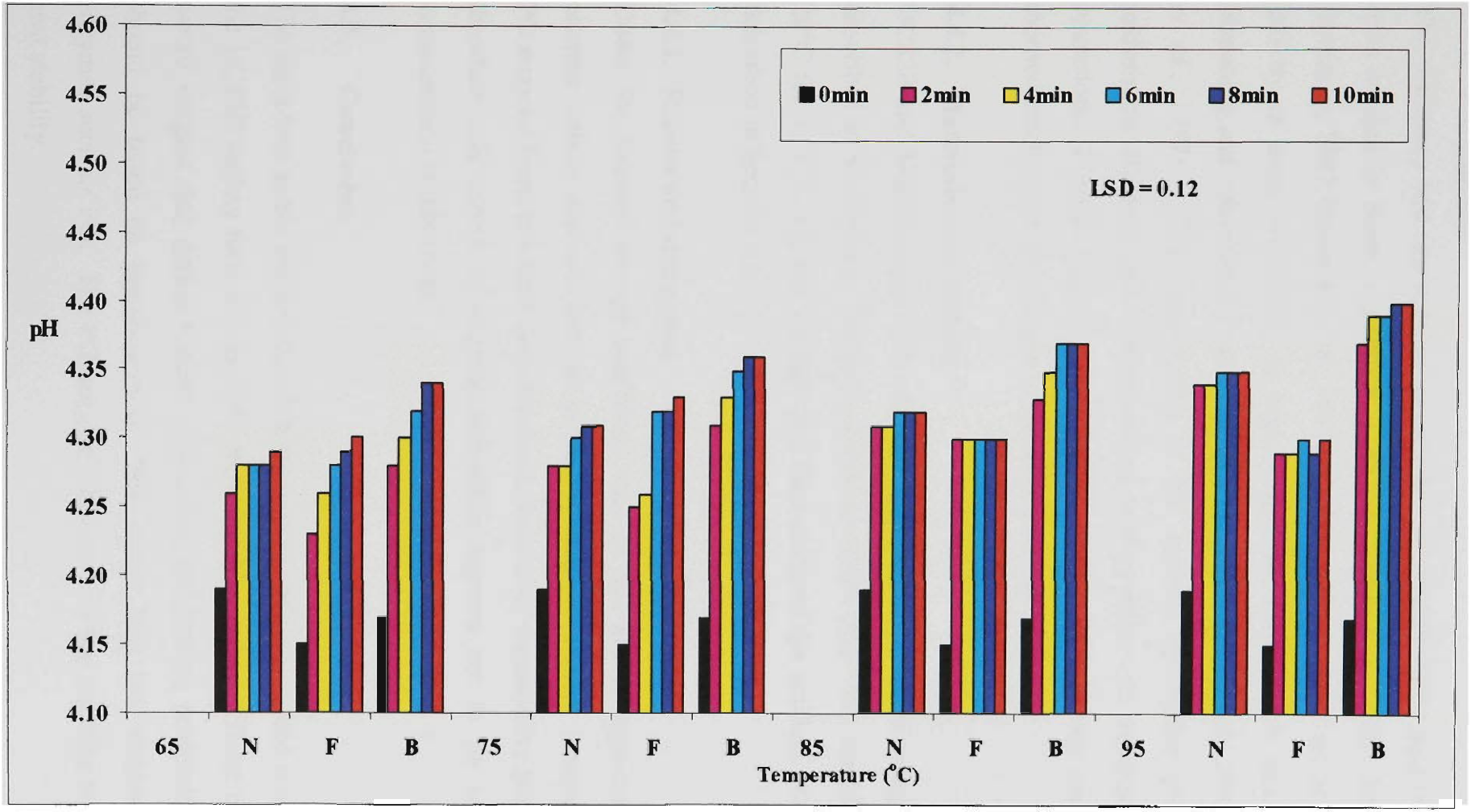


Figure 4.15 pH of thermally treated pulp prepared from fresh (N), frozen (F) and blanched (B) Alta tomatoes

4.4. Regeneration of enzymes after thermal inactivation

4.4.1. Introduction

The resistance and regeneration of enzymes such as PO after heat treatment has been studied in many vegetables (Aparicio-Cuesta *et al.*, 1992; McLellan and Robinson, 1987; Roderigo *et al.*, 1997). Although there is absence of residual PO activity in most vegetables, in some vegetables regeneration can occur after blanching and subsequent frozen storage (Aparicio-Cuesta *et al.*, 1992; Roderigo *et al.*, 1997). This regeneration of PO enzyme can cause production of undesirable flavours and odours during concentration and subsequent storage operations. For this reason the residual PO enzyme activity was measured after thermal inactivation and storage at suitable temperatures.

4.4.2. Materials and methods

UC82B and Alta tomatoes were macerated and thermally treated using the method described in Section 3.2. Portions of this macerated pulp were stored at 4°C and 20°C for 1, 3, 7, 14, and 28 days and then analysed for residual PO activity as described in Section 3.2.1.2.

4.4.3. Results and discussion

Under the selected storage conditions used in this study, regeneration of PO enzyme activity was not observed in the two varieties studied. It appears that the PO enzyme from tomatoes does not have observable regenerative properties and therefore this aspect of enzyme behaviour appears not to be an issue for consideration in this study.

4.5. Conclusion

The most heat stable enzyme found in the tomato varieties studied was PME from the UC82B variety followed by PME from the Alta variety. These observations would suggest that during tomato processing, the thermal processing schedule should be based on inactivation of PME rather than conventional indicator enzymes such as PO. The PG enzyme from both of the varieties had the same heat stability.

As expected the blanched tomatoes had considerably lower PO, PME and PG activities than the fresh or frozen tomatoes ($P \leq 0.05$). The freezing process was more effective in reducing the level of PO enzyme activity than the PME enzyme activity. By freezing, the PO enzyme activity was reduced by 38% in the UC82B variety and by 53% in the Alta variety, however the PME enzyme activities were only reduced by 2% and by 18% in the UC82B and Alta varieties respectively ($P \leq 0.05$). The freezing process appeared to enhance the PG enzyme activity and requires further research. During this study the blanching process reduced the enzyme activities of all three enzymes PO, PME and PG by 80%, 75% and 55% respectively.

These observations suggest that a short pre-blanch process may help shorten the duration and the intensity of the subsequent thermal break process. This approach may help reduce the overall thermal damage to heat sensitive flavour components in tomato and hence improve the sensory attributes of the final products. However the cumulative thermal effects of any pre-blanching and break processes would need to be considered in establishing an overall thermal processing protocol. The pH and acidity changes noted in processed tomatoes appear to be related to the extent and rate of inactivation of PME and PG enzymes. However, more extensive studies need to be carried out to confirm these observations. The changes in the pH and titratable acidity may have implications for subsequent processing and the need or otherwise to adjust final product acidity and pH by acid addition to achieve the required product specifications.

In summary, the heat stability of enzymes in Roma tomatoes decreased in the following order:

PME, UC82B > PME, Alta > PG, UC82B = PG, Alta > PO, UC82B > PO, Alta

CHAPTER 5

Clarification and prefiltration of tomato juice

5.1. Clarification by centrifugation

5.1.1. Introduction

Juice clarification involves the separation of suspended solids from the serum component by use of centrifugal force or filtration techniques. Conventional extraction methods have traditionally involved the use of mechanical presses and press aids. However, decantation and centrifugation are alternative methods that can be used in both juice extraction and clarification and there has been an increasing use of decanters and centrifuges by the juice industry in recent years; although, published information on operational parameters is limited. Current techniques involving decanters can potentially produce juice yields of 85-90 % without the use of press aids (Beveridge *et al.*, 1988). Modern decanters can also process over-ripe and thermally treated fruit mashes, which are difficult to do using conventional presses (Beveridge *et al.*, 1992). Clarification of fruit juices such as pineapple, apple and pear is now quite common on a commercial scale but tomato juice has rarely been clarified.

The purpose of the juice clarification step in this study was to fractionate the tomato solids from the serum component of the juice. This primary clarification step was achieved by centrifugation. The separated tomato solids were stored below -18°C and the serum fraction was clarified further by secondary filtration techniques involving microfiltration or ultrafiltration. Clarification of the juice was necessary because the membrane processes, such as RO and IMD, which were used for subsequent concentration of the juice, operate more effectively with clarified feeds. Indeed, the IMD membrane materials currently available effectively can only process clarified fruit juices.

5.1.2. Materials and methods

For the purpose of this work, the freezing and blanching processes were performed only on tomatoes of the UC82B variety, which were processed into

juice at break temperatures of 85°C and 95°C according to the method described in Section 3.2. The tomato juice was clarified by centrifugation according to the process described in Section 3.5.1. The clarified serum was stored overnight at 4°C pending further processing by secondary clarification techniques involving microfiltration or ultrafiltration as described in Section 3.5.2. The solids fraction was combined with the MF and UF concentrates obtained from the secondary clarification step and stored below -18°C until required for recombination studies. Soluble solids, suspended solids and total solids contents were determined according to Sections 3.3.2.4, 3.3.2.6 and 3.3.2.8 respectively. The viscosities of both clarified serum and juice were measured at 20°C using the method described in Section 3.3.1.3.

5.1.3. Results and discussion

Tomato juice prepared at 95°C break temperature had a slightly higher total solids level ($P \leq 0.05$) than the 85°C break juice (Table 5.1). After clarification, the 95°C serum had slightly higher total solids level, however the 95°C solids fraction had approximately 10% higher total solids content than the 85°C solids fraction ($P \leq 0.05$). The suspended solids level was also approximately 20% higher in the 95°C break serum than in the 85°C break serum ($P \leq 0.05$). These trends could be due to more juice components being extracted at higher temperatures as proposed by Luh and Daoud (1971). Similarly the viscosities of the 95°C juice and serum were approximately 5% and 7% higher respectively than the 85°C juice and serum (Table 5.1), reflecting the higher total solids level in the initial juice sample ($P \leq 0.05$). The higher viscosity of the 95°C serum may impact adversely i.e. reduce the flux rate, during subsequent RO and MF operations. Overall the serum component obtained from the centrifugation process still had a high level of suspended solids and required secondary clarification by either microfiltration or ultrafiltration. The solids component was stored below -18°C until required in the recombination stage.

Table 5.1 Composition of tomato juice and juice fractions prepared at 85°C and 95°C break temperatures

Sample	Total Solids (% w/w)	Soluble Solids (°Brix)	Suspended Solids (% w/w)	Viscosity (mPa.s)
Tomato juice 85°C break	5.49	4.80	1.42	590
Tomato juice 95°C break	5.57	4.90	1.48	620
Serum fraction 85°C break	5.15	5.00	1.05	310
Serum fraction 95°C break	5.20	5.00	1.25	330
Solids fraction 85°C break	10.07	-	-	-
Solids fraction 95°C break	11.27	-	-	-

Standard errors: total solids ± 0.35; soluble solids ± 0.52; suspended solids ± 0.42; viscosity ± 5.6

5.2. Clarification by microfiltration and ultrafiltration

5.2.1. Introduction

Microfiltration (MF) and ultrafiltration (UF) are preferred processes for clarification of fruit juices (De Carvalho *et al.*, 1998; Gokmen *et al.*, 1998). The advantages of UF and MF over conventional methods include the absence or need for filtering aids, reduction in energy consumption (since operated without requirement for steam) and lower labor requirements due to the simplicity of the process (Rao *et al.*, 1987). The effectiveness of MF and UF processes in juice clarification is entirely dependent on factors such as the membrane type, the pore size and the resulting flux (Fukamoto *et al.*, 1998). The disadvantage of UF and MF use is the development of haze if the process is not properly implemented. Usually the larger the pore size the greater the risk of haze development due to the passage of low molecular polyphenolic compounds (Fukamoto *et al.*, 1998). The use of UF and MF for clarification of fruit juices such as pear (Kirk *et al.*, 1983), grapefruit (Hernandez *et al.*, 1992), orange (Johnson *et al.*, 1996) and apple (Thomas *et al.*, 1986) is quite common whereas clarification of tomato juice has gained little attention. This may be due to the high level of suspended solids naturally present in tomato juice and the absence of any real reason for separating the pulp from the serum since tomato juice is normally concentrated by thermal vacuum evaporation processes. Furthermore consumer perceptions and

expectations of tomato juice is that it is a cloudy or non-clarified juice. This study sought to determine the feasibility of using MF and UF membrane processes for the secondary clarification of the serum produced from primary separation of tomato juice by centrifugation.

5.2.2. Materials and methods

Tomato serum from juice, processed at break temperatures of 85°C and 95°C, of the UC82B variety was prepared by centrifugation according to Section 3.5.1. UF and MF processes using the membranes and operating parameters detailed in Section 3.5.2 were then used to process the serum. The UF and MF permeates were used for subsequent preconcentration and concentration by RO and IMD respectively. The UF and MF concentrates were frozen below -18°C and were used for subsequent recombination studies. The membrane flux was measured at two temperatures, viz. 10°C and 40°C and graphs of flux rate ($L.m^{-2}.h^{-1}$) *vs* time (min) were plotted for the serum samples. The two temperatures were selected because flux rates are affected by processing temperatures and generally higher processing temperatures give better flux rates. The lower temperature was selected to retain quality and minimise microbial growth. The higher temperature of 40°C would give better flux rates and is closer to what is used commercially. The suspended solids and total solids contents were measured as described in Sections 3.3.2.6 and 3.3.2.8 respectively. The viscosity was measured according to the method given in Section 3.3.1.3.

5.2.3. Results and discussion

The MF and UF processes successfully removed most of the suspended solids from the pre-clarified tomato serum and therefore either process would appear suitable for secondary clarification. The MF permeates contained slightly higher suspended solids ($P \leq 0.05$) than the UF permeates (Table 5.2) reflecting the larger membrane pore size used for MF processing. Overall, the 95°C break permeates had marginally higher suspended and total solids levels than the 85°C break permeate samples which was probably due to the higher suspended and total solids levels in the initial 95°C break serum (see Table 5.1). The lower suspended

and total solids levels in the UF permeates could also account for the lower viscosities of the UF permeates compared to those from MF.

Table 5.2 Total solids, soluble solids, suspended solids and viscosity of MF and UF concentrates and permeates

Sample	Total Solids (% w/w)	Soluble Solids (°Brix)	Suspended Solids (% w/w)	Viscosity (mPa.s)
MF 85°C break permeate	4.20	4.20	0.20	260
MF 85°C break concentrate	5.00	5.00	1.75	-
MF 95°C break permeate	4.32	4.30	0.22	280
MF 95°C break concentrate	5.10	5.00	1.90	-
UF 85°C break permeate	4.12	4.10	0.10	240
UF 85°C break concentrate	5.39	5.30	1.85	-
UF 95°C break permeate	4.20	4.20	0.15	250
UF 95°C break concentrate	5.45	5.40	1.95	-

Standard errors: total solids ± 0.66; soluble solids ± 0.33; suspended solids ± 0.40, viscosity ± 9.2

The flux rate usually measures the performance of the membranes. A comparison of the MF and UF processes at the same temperature indicated that the MF process had better flux rates ($P \leq 0.05$) than the UF process (Figures 5.1 and 5.2). This was due to the larger pore size of the MF membrane. Similar clarification studies done on tangerine juice showed that the larger membrane pore size of 0.1μm had better flux rate than smaller pore sizes of MWCO 25,000, MWCO 50,000 and MWCO 100,000 (Chomchong and Noomhorm, 1991). Also, for any given process and processing temperature, there were little or no differences in flux rates of the juices processed at the two different break temperatures of 85°C and 95°C. As indicated by Figures 5.3 and 5.4, the MF and UF processes operated at 40°C gave better flux rates than at 10°C ($P \leq 0.05$).

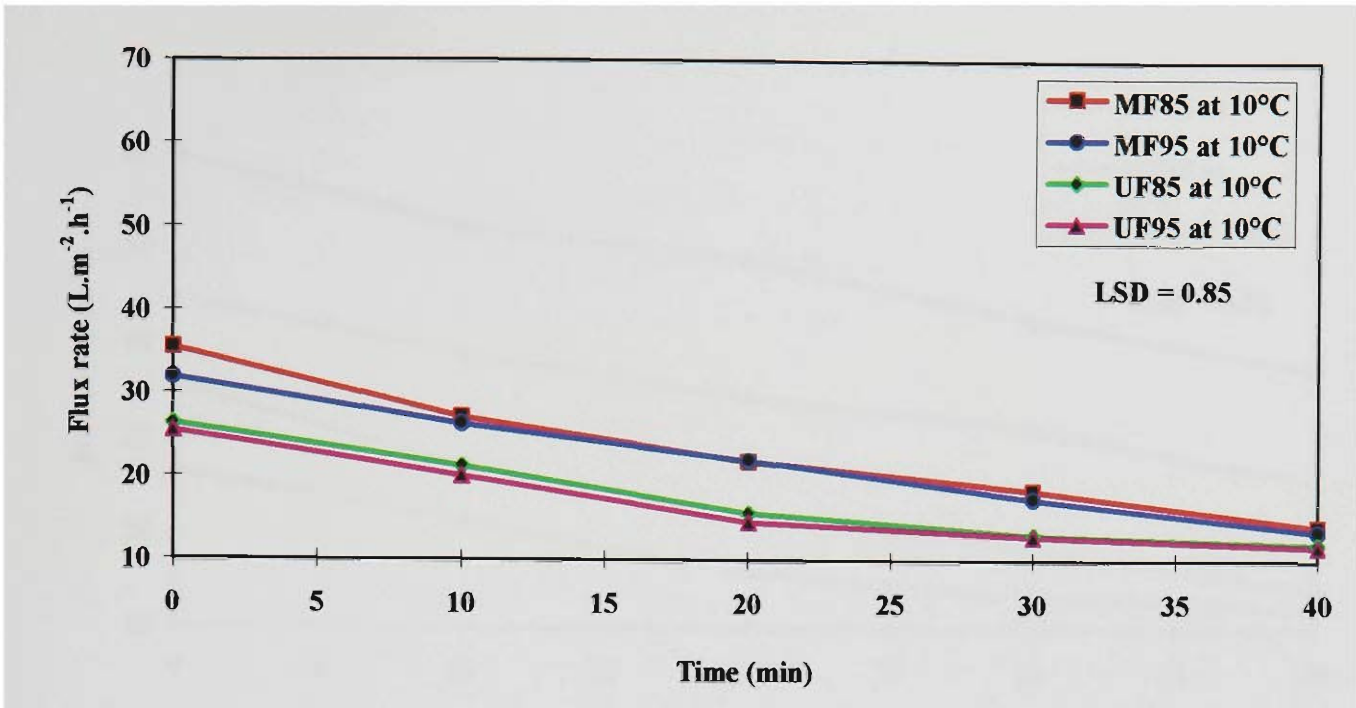


Figure 5.1 **Change in flux rate with time during microfiltration and ultrafiltration of 85°C and 95°C break tomato serums processed at 10°C**

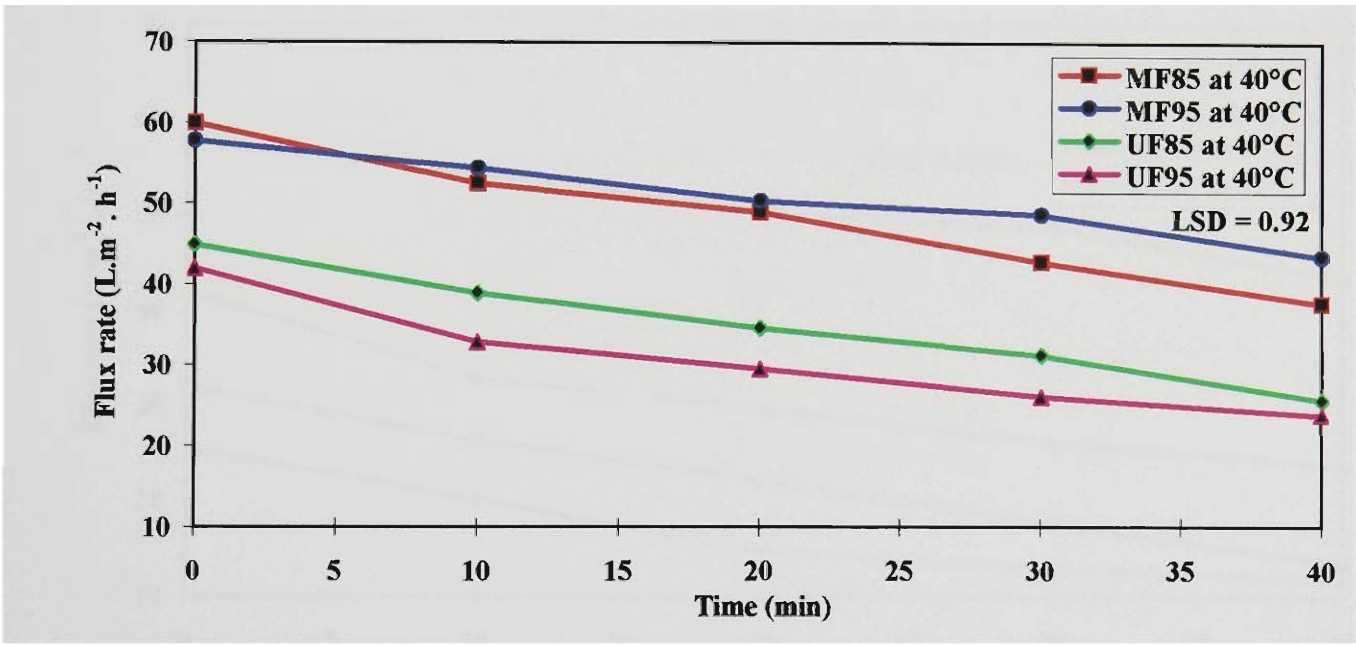


Figure 5.2 **Change in flux rate with time during microfiltration and ultrafiltration of 85°C and 95°C break tomato serums processed at 40°C**

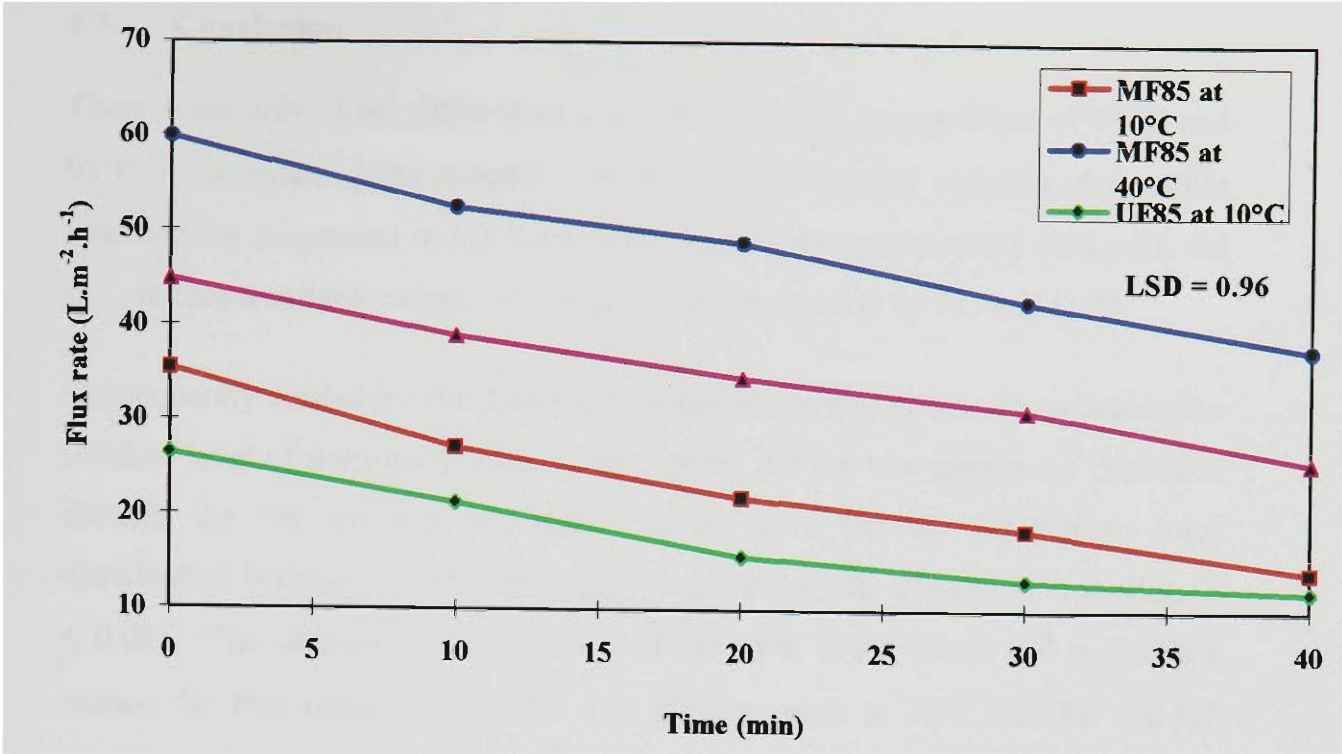


Figure 5.3 Change in flux rate with time during microfiltration and ultrafiltration of 85°C break tomato serum processed at 10°C and 40°C

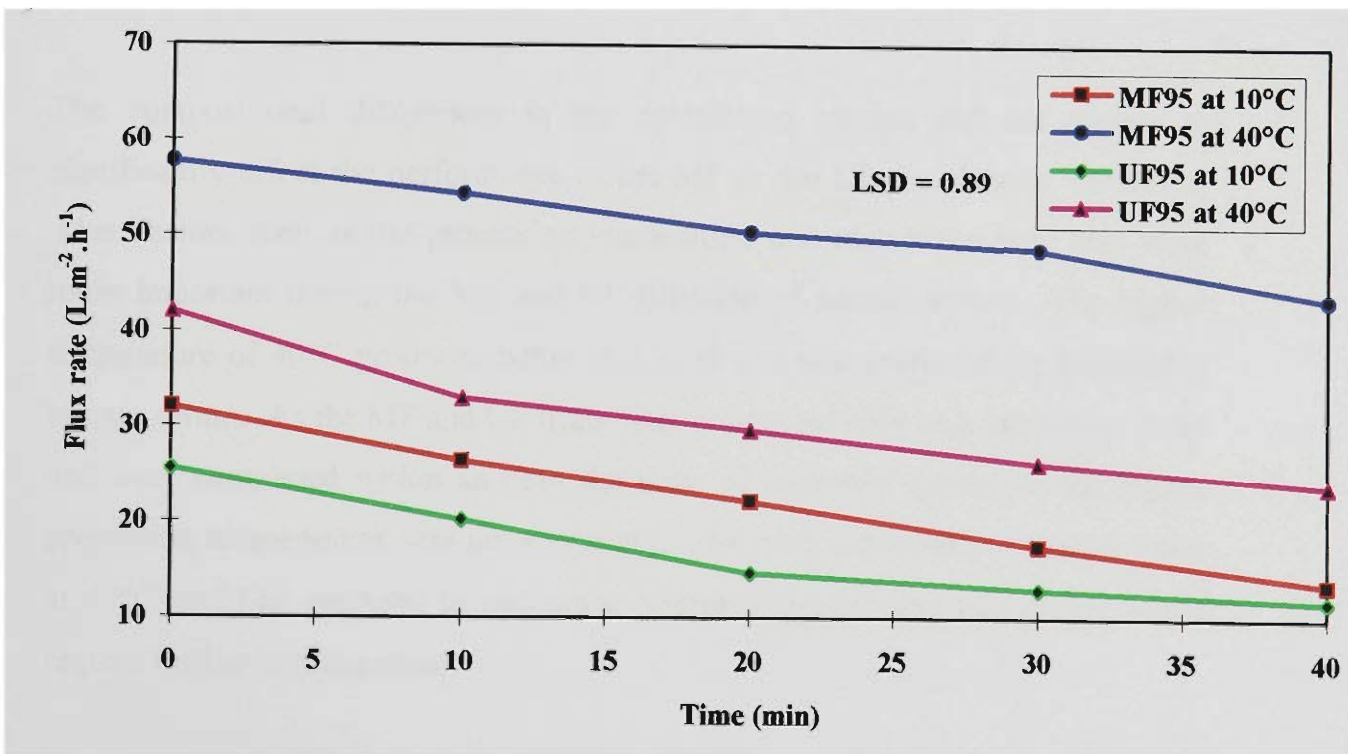


Figure 5.4 Change in flux rate with time during microfiltration and ultrafiltration of 95°C break tomato serum processed at 10°C and 40°C

5.3. Conclusion

There were only slight differences between the solids composition of 85°C and 95°C break tomato juice samples. Primary clarification by centrifugation, while reducing the suspended solids level in the serum by approximately 50%, still did not produce a suitable serum for subsequent concentration by RO and IMD.

Consequently secondary clarification by membranes was necessary to reduce the residual level of suspended solids in the serum. Of the two membrane processes chosen, the MF process was found to be more suitable for tomato juice clarification because it produced better flux rates and was less prone to fouling ($P \leq 0.05$). The slightly higher viscosity of the 95°C break serum did marginally reduce the flux rates for both MF and UF processes at 10°C and for the UF process at 40°C compared to the 85°C break serum under the same conditions (see Figures 5.1 and 5.2). For the MF process at 40°C the viscosity difference did not appear to influence the flux rate and indeed the 95°C break serum showed higher flux rates than the 85°C break serum ($P \leq 0.05$).

The compositional differences in the centrifuged serums did not appear to significantly affect the performance of the MF or the UF membranes. However, other factors such as the processing temperature and membrane pore size were more important during the MF and UF filtration of tomato serum. The higher temperature of 40°C produced better flux rates and was preferred for processing tomato serum. As the MF and UF trials were conducted only on a laboratory scale and were completed within an hour the issue of microbial growth at the higher processing temperatures was not a concern. However extended processing times at 40°C could be expected to encourage microbial growth and this aspect would require further investigation.

CHAPTER 6

Preconcentration and Concentration of Tomato Serum

Tomato juice is traditionally concentrated by thermal vacuum evaporation (TVE) processes. The use of high temperature and continuous recirculation of tomato juice during TVE can often lead to deterioration in flavour, colour and volatile aroma of the final tomato concentrates. The application of low temperature membrane concentration techniques can help reduce some of the undesirable thermal changes commonly associated with high temperature processing. The aim of this study was to evaluate the use of linked membrane processes such as microfiltration (MF) or ultrafiltration (UF), with reverse osmosis (RO) and isothermal membrane distillation (IMD) for the clarification, preconcentration and concentration of tomato juice to produce final concentrates of improved colour, flavour and aroma. Two such linked processes are illustrated in Figure 6.1.

6.1. Preconcentration by reverse osmosis

6.1.1. Introduction

The RO process was originally used for desalination of seawater and as the process became better understood its application extended to concentration of liquid foods. Although RO is still primarily used for purification of water, its use in fruit juice concentration is well documented (Braddock *et al.*, 1988; Bowden and Isaacs, 1989; Kane *et al.*, 1995). The advantage of concentration by RO is that no phase change occurs during concentration hence the delicate flavours and aromas of heat sensitive food products can be preserved (Chou *et al.*, 1991; Kane *et al.*, 1995; Olle *et al.*, 1997). Generally RO is used more for preconcentration rather than for concentration and this is due to the low total solids achieved by the RO process. The low total solids level achieved is due to the diminishing flux rate. Preconcentration by RO prior to TVE processes also has advantages such as reduction in energy costs, shorter processing times and increase in production capacity (Dale *et al.*, 1982). The low temperatures used during RO concentration can also alleviate the formation of browning compounds such as furfural and hydroxymethylfurfural, which affect the final colour of tomato pastes.

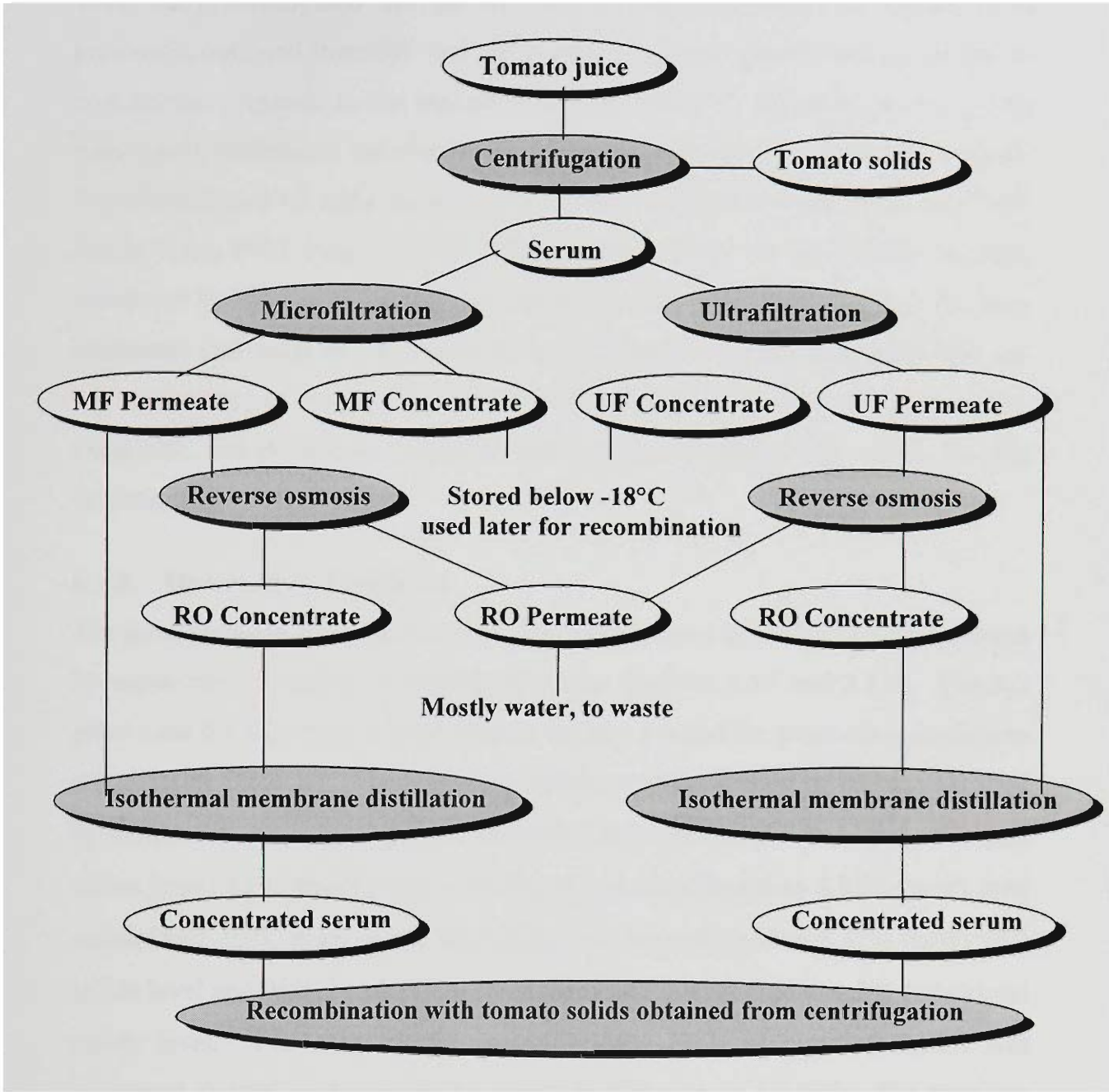


Figure 6.1 **Clarification, preconcentration and concentration of tomato serum by linked membrane processes**

This study investigated the use of RO for preconcentration of tomato juice permeates obtained from MF and UF processes. The objective was to use RO to concentrate permeate to the highest total solids level so that the duration of the subsequent isothermal membrane distillation (IMD) process could be reduced. Preconcentration of other juices by RO is well documented (Merlo *et al.*, 1986; Zhang *et al.*, 1992; Ramteke *et al.*, 1993; Walker, 1990), but tomato juice is rarely processed by RO due to the high level of suspended solids present. Since the juice permeates had most of the suspended solids removed by centrifugation, MF and UF processes, an expensive tubular RO plant was unnecessary and a less expensive spiral wound brackish water RO membrane was used for the investigation.

6.1.2. Materials and methods

The juice permeates used as the RO feed were obtained by centrifugation followed by either microfiltration of ultrafiltration (see Sections 3.5.1 and 3.5.2). The RO plant used for this study is described in Section 3.6 and the processing conditions are given in Table 3.3. The following samples were processed by RO as described in Section 3.6: 85°C break juice, centrifuged and microfiltered to 4.2% (w/w) total solids level; 85°C break juice, centrifuged and ultrafiltered to 4.12% (w/w) total solids level; 95°C break juice, centrifuged and microfiltered to 4.32% (w/w) total solids level and 95°C break juice, centrifuged and ultrafiltered to 4.2% (w/w) total solids level. For each sample approximately 10 L of clarified serum was processed at 10°C and the sample was kept chilled in an ice bath. The flux rate ($L.m^{-2}.h^{-1}$) was calculated as described in Section 3.5.2.

The soluble solids and total solids contents of the RO concentrate and permeate were determined as described in Sections 3.3.2.4 and 3.3.2.8 respectively. To determine whether sugars had passed through the membrane, the RO permeate was analysed for residual glucose and fructose levels as per Section 3.3.2.5. The RO flux rate ($L.m^{-2}.h^{-1}$) data was plotted as a function of time (min) for samples from the two break temperatures, 85°C and 95°C and for both MF and UF juice permeates. This experiment was repeated three times and the mean results were

plotted on a graph of the flux rate ($L.m^{-2}.h^{-1}$) versus soluble solids content for all the samples processed by RO.

6.1.3. Results and discussion

During RO preconcentration of the MF or UF clarified serums, the flux rate decreased with time. This phenomenon is due to the increase in the total solids content of the recirculating feed and is common to both hydrophobic and hydrophilic membrane processing. As shown in Figure 6.2, the clarified serums (both MF and UF) from the lower break temperature juice serums (85°C) had higher initial flux rates than the high break temperature juice serums ($P \leq 0.05$). This was due to the lower total solids content of the lower break temperature (85°C) juice serums (Table 5.1). Also, the UF clarified serums had better RO flux rates for both 85°C and 95°C break samples than the corresponding MF clarified serums (Figure 6.3) and this was also due to the lower total solids content of these clarified serums ($P \leq 0.05$). The lower total solids contents of the UF clarified serums was due to the smaller pore size of the UF membrane which consequently retained larger molecules than the MF membrane. Although MF gave better flux rates than UF during secondary clarification of serum, the UF clarified serums gave better RO flux rates than MF clarified serums during RO processing ($P \leq 0.05$). Consequently the UF process may be better overall for serum clarification and subsequent RO preconcentration than the corresponding MF process.

Since the RO permeate fraction was to be discarded, it was necessary to check process losses by investigating the soluble solids that may have permeated the membrane. The most common solutes that permeate RO membranes are sugars such as glucose and fructose. The RO permeates in this study were found to contain both glucose and fructose (see Table 6.1). Also the RO permeates from the MF clarified serums had higher sugar permeation rates than the corresponding RO permeates from UF clarified serums ($P \leq 0.05$). This may be related to the higher initial soluble solids content of the MF juice permeates.

Table 6.1 Solids and sugar contents of tomato juice concentrates and permeates produced by RO of MF and UF clarified juice serum

Sample	Soluble Solids (°Brix)	Total Solids (% w/w)	Glucose (g/L)	Fructose (g/L)
85°C break MF/RO permeate [1]	*	0.03	0.09	0.06
85°C break MF/RO concentrate [2]	8.38	8.54	N/A	N/A
85°C break UF/RO permeate [3]	*	0.05	0.07	0.05
85°C break UF/RO concentrate [4]	8.30	8.41	N/A	N/A
95°C break MF/RO permeate [5]	*	0.05	0.10	0.07
95°C break MF/RO concentrate [6]	8.56	8.66	N/A	N/A
95°C break UF/RO permeate [7]	*	0.06	0.05	0.05
95°C break UF/RO concentrate [8]	8.48	8.59	N/A	N/A

* Below the measurable limit of the refractometer method used.
Standard errors: soluble solids ± 0.78; total solids ± 0.38; glucose ± 0.05; fructose ± 0.07

Key:
1 - Permeate produced from 85°C break serum clarified by MF then preconcentrated by RO
2 - Concentrate produced from 85°C break serum clarified by MF then preconcentrated by RO
3 - Permeate produced from 85°C break serum clarified by UF then preconcentrated by RO
4 - Concentrate produced from 85°C break serum clarified by UF then preconcentrated by RO
5 - Permeate produced from 95°C break serum clarified by MF then preconcentrated by RO
6 - Concentrate produced from 95°C break serum clarified by MF then preconcentrated by RO
7 - Permeate produced from 95°C break serum clarified by UF then preconcentrated by RO
8 - Concentrate produced from 95°C break serum clarified by UF then preconcentrated by RO

The RO process has been shown to be feasible for concentration of a variety of fruit juices (Koseoglu *et al.*, 1990; Walker, 1990; Chou *et al.*, 1991; Das Gupta and Jayarama, 1996;) but this present study would suggest it is not well suited to the preconcentration of tomato juice since it can only achieve relatively low concentration levels (around 8.5% w/w total solids content). Most of the earlier RO studies on tomato juice reported similar concentration levels to those achieved in this present study (Pepper *et al.*, 1985; Merlo *et al.*, 1986). Although the concentration factor in this study was only approximately 2-fold, the RO process can concentrate to a higher solids level and one particular study showed that processing tomato juice using a tubular RO system gave a solids level of 20%

(Yildiz *et al.*, 1993). Financial constraints restricted this project to the use of a spiral RO system, which could only concentrate the primary juice to a maximum of 8.5% w/w total solids content. This was not considered to be a major concern because further concentration was to be achieved using the IMD process.

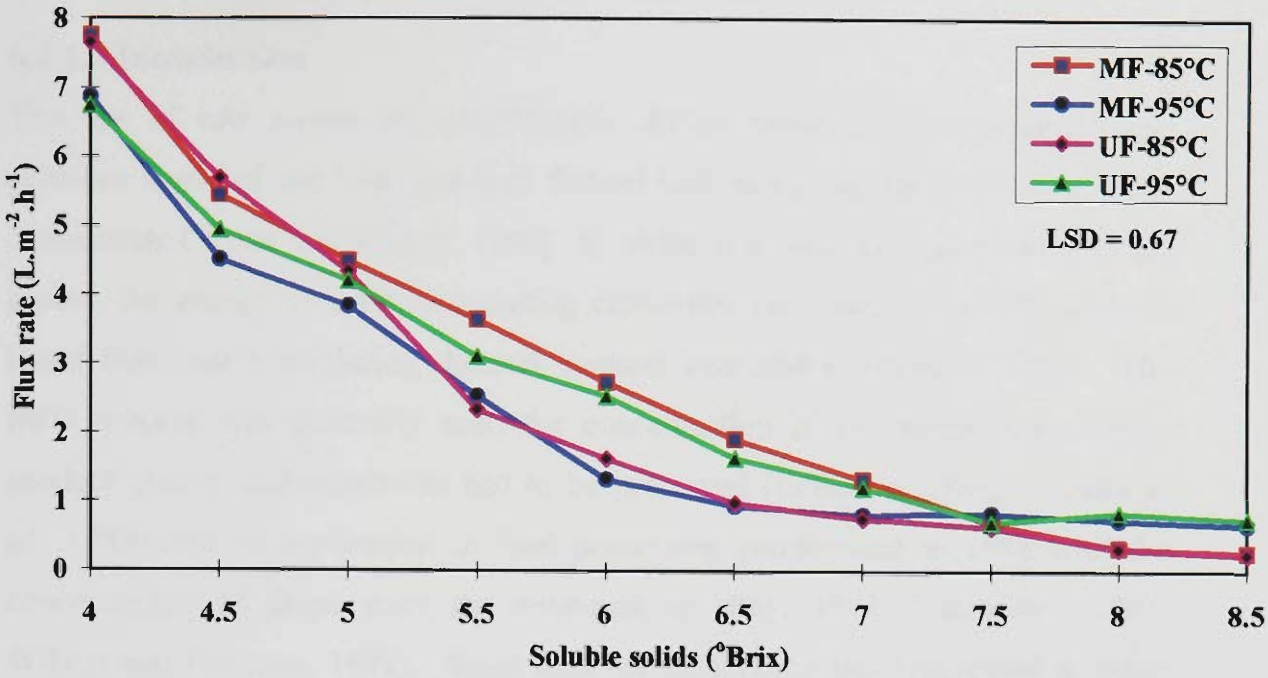


Figure 6.2 Change in flux rate with increasing soluble solids contents during preconcentration of MF and UF clarified tomato serum by RO

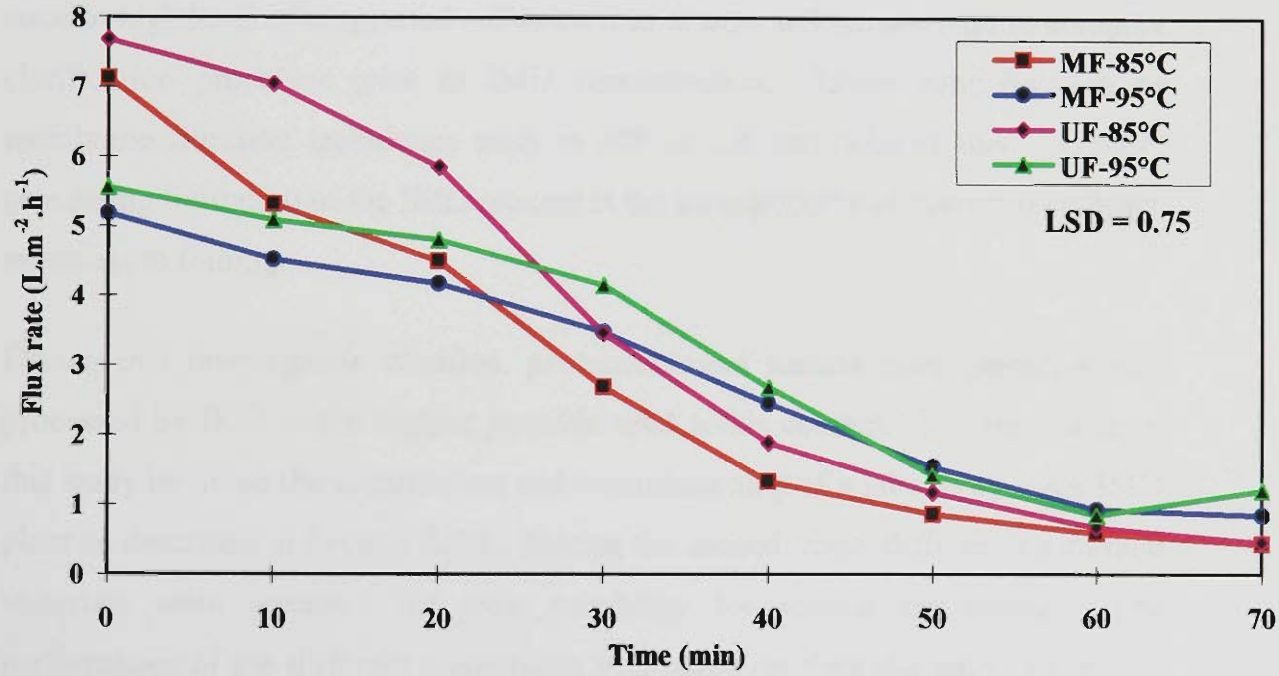


Figure 6.3 Change in flux rate with time during preconcentration of MF and UF clarified tomato serum by RO

6.2. Concentration by isothermal membrane distillation

6.2.1. Introduction

The use of low processing temperatures during membrane concentration can preserve some of the heat sensitive flavour and aroma compounds in the final concentrate (Wong and Winger, 1999). In addition to enhancement of flavour and aroma, the energy consumption during membrane concentration is substantially lower than that used during thermal vacuum evaporation (Pepper, 1990). The IMD process was primarily used for concentration of pharmaceuticals where product quality and sensitivity had to be preserved (Lefebvre, 1986; Johnson *et al.*, 1989) and its application in food processing commenced in 1986 with the concentration of grape juice for wine-making (Ray, 1991; Thompson, 1991; Wilson and Peterson, 1992). Since then the technology has progressed to other fruit juices such as apple, orange and tomato (Sheng *et al.*, 1991; Petrotos *et al.*, 1998). Although IMD can produce concentrates of superior sensory quality, the IMD process can concentrate only clarified juices. Fruit juices containing low suspended solids such as grape are simple to concentrate. However, juices that contain high level of suspended solids such as orange and tomato require complex clarification processes prior to IMD concentration. Either centrifugation or membrane filtration techniques such as MF or UF can achieve this. Another processing limitation of the IMD process is the susceptibility of current membrane materials to fouling.

During this investigation clarified, preconcentrated tomato juice permeate was processed by IMD to the highest possible total solids content. The first stage of this study involved the construction and commissioning of a laboratory scale IMD plant as described in Section 3.7.1. During the second stage, different membrane materials were screened for their suitability for tomato processing. The performance of the different membranes was based on their durability to tomato juice processing and maintenance of the flux rate. The third stage involved IMD concentration trials on the preconcentrated tomato juice serums to produce concentrates of the highest possible total solids level. The final stage involved establishing suitable cleaning and sanitation procedures for the IMD membranes.

6.2.2. Materials and methods

The clarified, RO preconcentrated juice serums were obtained as described in Sections 3.5 and 3.6. Only RO serums from the UC82B variety processed at 85°C and 95°C break temperatures were used for concentration by the laboratory IMD plant described in Section 3.7. The IMD membranes used, the samples concentrated and the processing conditions employed are given in Tables 3.5, 3.6 and 3.7 respectively. The flux rate was measured as described in Section 3.7.2.

6.2.2.1. Effect of membrane type

Clarified, preconcentrated juice serums were processed using the five different membrane types described in Table 3.5. Some of these membranes were made of the same material but differed in pore size and thickness. Five IMD trials were conducted for each membrane type using the parameters given in Table 3.7 and the mean flux rate ($kg.m^{-2}.h^{-1}$) versus processing time (min) was plotted for each membrane type. The most suitable membrane was selected on the basis of flux rate performance and the durability to tomato juice processing. The selected membrane (Goretex XP 98007) was then used for subsequent processing trials and cleaning studies as detailed in Sections 6.2.2.2, 6.2.2.3 and 6.2.2.4.

6.2.2.2. Effect of feed temperature on IMD performance

The primary and secondary clarified, RO preconcentrated tomato serums (i.e MF-RO and UF-RO linked from 85°C and 95°C break temperatures) were processed at two different temperatures, viz. 10°C and 25°C. The temperature of the brine solution was maintained at 25°C. The flux rates were measured hourly as described in Section 3.7.2.

6.2.2.3. Effect of feed concentration on IMD performance

Clarified and clarified-RO preconcentrated tomato serums of different total solids contents, viz. 4.5% (w/w) and 8.5% (w/w) were processed by IMD. The 4.5% (w/w) total solids juice serum was obtained by primary clarification using a centrifugation process followed by secondary clarification by either MF or UF membrane processes as described in Sections 3.5.1 and 3.5.2. The 8.5% (w/w)

total solids juice serum was obtained by primary centrifugation followed by linked membrane processing by either, MF-RO or UF-RO processes as described in Sections 3.5.1, 3.5.2 and 3.6. The soluble solids and total solids contents of the IMD concentrates were measured as described in Sections 3.3.2.4 and 3.3.2.8 respectively. The feed and concentrate viscosity during processing was measured according to the method described in Section 3.3.1.3.

6.2.2.4. Cleaning studies

Initially ten different cleaning agents, as described in Section 3.7.3.1, were used for cleaning the selected membrane. The soiled membrane used in these cleaning trials was a Gortex XP 98007 membrane following 10 hours of processing of UF-RO linked tomato serum from 95°C break temperature juice. The cleaning agent best suited to the selected membrane was a 1% (w/v) NaOH solution and this was subsequently used for routine cleaning of the plant.

6.2.3. Results and discussion

During IMD processing, variations in membrane type (material, pore size and thickness), juice concentration, juice temperature, brine concentration and brine temperature can significantly affect the rate of water removal. During this study only three of these variables were investigated viz. membrane type, juice concentration and juice temperature. The temperature and concentration of the brine stripper solution were kept constant at 25°C and 50% (w/w) respectively.

6.2.3.1. Effect of membrane type

As in hydrophilic membrane processing, membrane performance during hydrophobic membrane processing (IMD) is measured by the flux rate. The flux rate decreased with processing time, which was due to the increase in the total solids content of the recirculating juice serum feed. The dependency of membrane performance on structural properties such as material, pore size and thickness is obvious during hydrophilic processing. Hydrophilic membranes of larger pore size tend to give better flux rates (Snir *et al.*, 1996; Constenla and Lozano, 1995). This was also observed during hydrophobic IMD processing. Of the two Goretex membranes, Goretex XP 98007, with the larger pore size of 0.45

μm, exhibited higher flux rates ($P \leq 0.05$) than the Goretex XP 98006 membrane of pore size 0.20 μm (Figure 6.4). In addition to better flux performance, the retention of volatile organic components such as 3-methylbutanal, ethyl hexanoate and limonene is higher for membranes with larger pore sizes (Barbe *et al.*, 1998).

For hydrophilic processing, membrane material can affect the rate of water removal. This was not obvious during hydrophobic IMD processing. For example, in relation to the membranes with the same porosities (see Table 3.5), although the Sumitomo WP 02-40 membrane, which is made of PTFE, had better flux rates than the Gelman 2TPR membrane which is a fluoroethylene copolymer, the Goretex XP 98006 membrane, which is also made of PTFE, had significantly lower initial flux rates than the Gelman 2TPR membrane ($P \leq 0.05$). The membrane performance also appeared to be unaffected by the thickness of the membrane, with the thicker Sumitomo membrane having better initial flux rates than the thinner Gelman 2TPR and Celgard 2500 membranes, or the similarly sized Gortex XP 98006 membrane.

The durability of some of the membranes investigated during extended IMD processing was a major concern. Membranes such as the Sumitomo WP 02-40 and Gelman 2TPR membranes performed better than the other membranes but were easily damaged during extended IMD processing. The poor durability of the Sumitomo membrane was due to the absence of backing material, an observation also reported by Johnson and Bailey (1994) during grape juice concentration work. Although there was a backing material present with the Gelman 2TPR membrane, it separated during extended IMD processing. Durham and Nguyen (1994) also reported the separation of the backing material of the Gelman 2TPR during cleaning of the membrane with a 1% (w/v) caustic solution.

In comparison to the other membranes, the Celgard 2500 membrane had extremely low flux rates and was unsuitable for tomato serum processing. The Sumitomo WP 02-40, Gelman 2TPR and Celguard 2500 membranes did not achieve the expected level of concentration of soluble solids. The highest level of

concentration (soluble solids content of 45°Brix) was achieved with the Goretex XP 98007 membrane. If the choice of membrane type to use was based on membrane material, it appears that PTFE was most suited to tomato processing. If the design and durability of the Sumitomo WP 02-40 and the Gelman 2TPR membranes is improved they may have scope for use in extended tomato juice processing, however, based on the present data it appears that the Goretex membrane at 0.45 μm pore size (Goretex XP 98007) is the most suitable for tomato processing.

In addition to the structural properties of the membrane, the design and configuration is also important for enhancing the performance of the membrane. Four common membrane configurations can be used for membrane systems: plate and frame, flat sheet, hollow fibre and spiral wound. The three most common configurations used for IMD processing have been hollow fibre, flat sheet and spiral wound and this study was carried out using a flat sheet configuration. Although the tubular configuration is more suitable for processing viscous feeds such as tomato, its use in IMD processing is not well documented. This may be due to the high capital costs associated with installation of tubular systems.

6.2.3.2. Effect of feed temperature on IMD performance

The effect of temperature on IMD performance was examined only on the feed side of the membrane at two temperatures, viz. 10°C and 25°C, using only the MF-RO and UF-RO linked feeds. The temperature of the brine was maintained at 25°C. The temperatures selected were based on previous IMD pilot studies on tomato juice concentration (Durham and Nguyen, 1994; Petrotos *et al.*, 1998). As expected, the flux rates were substantially higher when the juice serum was processed at the higher feed temperature (Figure 6.5). The better performance in the flux rates could be due to the higher kinetic energy of the water vapour molecules and the lower viscosity of the tomato serum feed. The serum processed at the lower temperature could only be concentrated to a maximum of 35 °Brix soluble solids due to the diminishing flux rate (Figure 6.6). Studies conducted by Sheng *et al.* (1991) on fruit juices also reported higher flux rates at higher

processing temperatures, although the temperatures used for their study (29 to 40°C) were substantially higher than those used in the present study. The higher the temperature, the higher the flux rate is also a common trend reported during hydrophilic membrane processing (Mengual *et al.*, 1993; Fukumoto *et al.*, 1998).

The lower IMD flux rates observed at 10°C could also be due to the temperature polarisation effect. Usually temperature polarisation is created by a thermal gradient on the two sides of the membrane and results in aggregation of solids near the feedside surface of the membrane. Since the temperature gradient between sample processed at 10°C and the brine (25°C) was greater than that with feed processed at 25°C, the feed processed at the lower temperature was more prone to temperature polarisation. Martinez-Diez and Vazquez-Gonzalez (1996) studied the effects of temperature polarisation of pure water during hydrophobic processing and concluded that some membranes are more prone to temperature polarisation than others. The effects of temperature polarisation were not studied in detail during this investigation.

The tomato serums clarified and preconcentrated from lower break temperature juices had slightly better IMD flux rates than their high break temperature counterparts when they were processed at 25°C than when processed at 10°C ($P \leq 0.05$) (Figure 6.5). At the higher IMD processing temperature, the UF-RO clarified, preconcentrated serums appeared to have better IMD flux rates and this could be due to the lower initial total solids content of these serums ($P \leq 0.05$). For this reason linked UF-RO processes may be more suitable processes for preparation of serum for IMD processing. The higher temperature of IMD processing could however also present a risk in terms of microbiological quality and for this reason the final products were assessed for microbiological quality.

6.2.3.3. Effect of feed concentration on IMD performance

The decline in flux rate during membrane concentration is a common occurrence during both hydrophilic and hydrophobic processing. This decline is mainly due to the increase in the soluble solids content and the increasing viscosity of the

serum during concentration (Figures 6.6 and 6.8 respectively). The flux rates observed during IMD processing of the serum obtained from the individual MF and UF processes were higher ($P \leq 0.05$) than those obtained for serum from the corresponding RO linked membrane processes (Figure 6.7). This was due to the lower initial soluble solids contents and thus lower viscosities of the MF and UF processed serums. Although the flux rates were better for the serums processed only by MF and UF than for those processed by linked MF-RO and UF-RO processes, the processing times required to achieve the same degree of concentration were longer and the desired final soluble solids content of 45°Brix was not achieved with these unit MF and UF processes. Furthermore, preconcentrating the juice serum by RO reduced the IMD processing time by 10 hours (Figure 6.7). This would be advantageous during commercial processing; however the economics and final product quality in terms of chemical and microbiological quality require further investigation. Although feed temperature and concentration significantly affected the IMD flux rate ($P \leq 0.05$), the initial break temperature of the tomato juice only marginally affected the IMD membrane performance with lower break temperatures giving better overall IMD flux rates for serums produced by MF-RO and UF-RO processes (Figures 6.6 and 6.7 respectively). The serum viscosity (Figure 6.8) followed an exponential trend, which meant that a slight increase in soluble solids content caused a significant increase in the juice retentate viscosity, which was responsible for the declining flux. The exponential increase in the viscosity also limited the achievable concentration level, which was found to be 45°Brix soluble solids content.

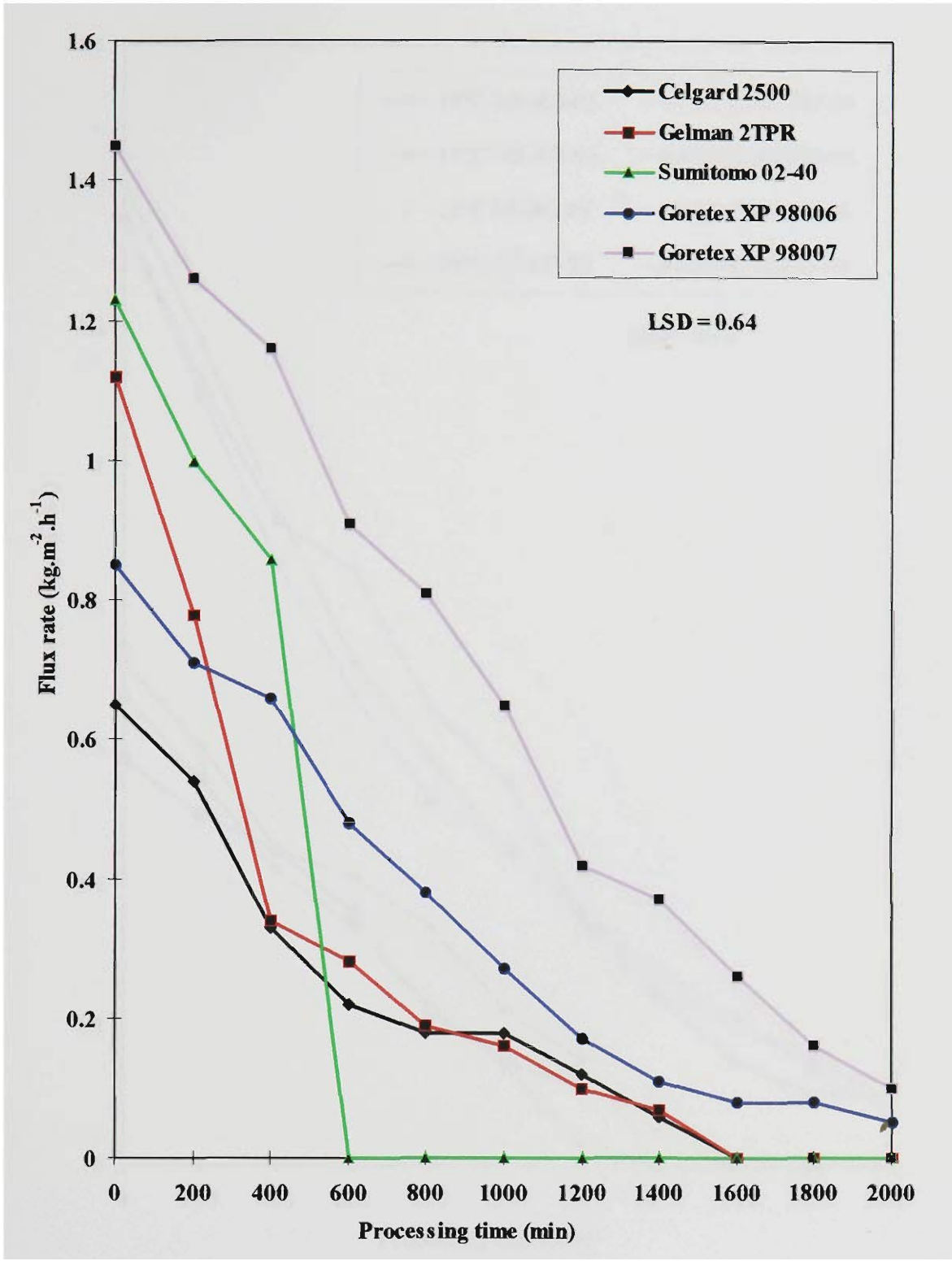


Figure 6.4 **Change in flux rate with time for different membrane types during IMD processing of clarified, preconcentrated tomato serum (8.54% w/w total solids)**

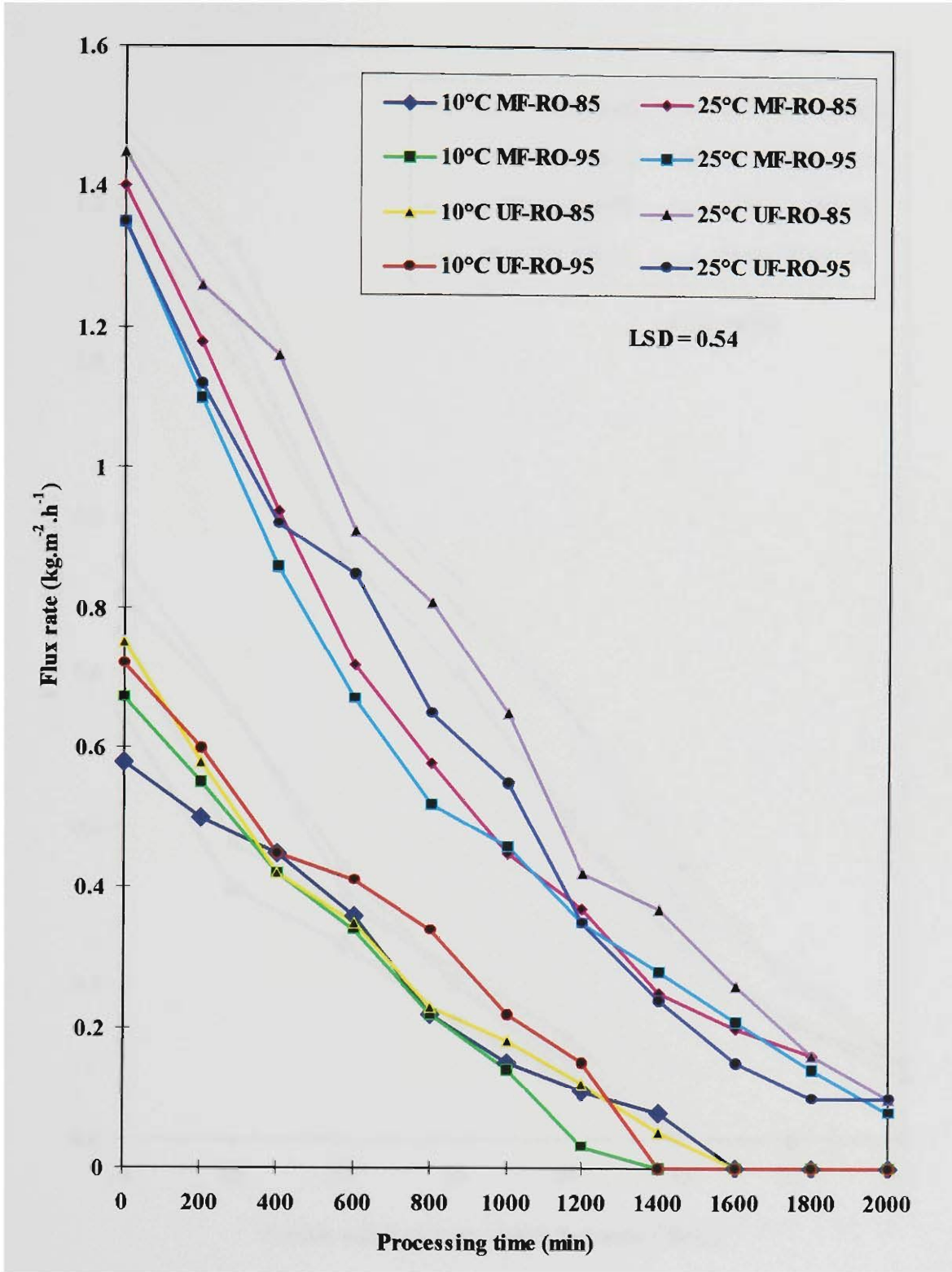


Figure 6.5 **Change in flux rate with time during IMD concentration of clarified, preconcentrated tomato serums at 10°C and 25°C feed temperatures using Gortex XP 98007 membrane**

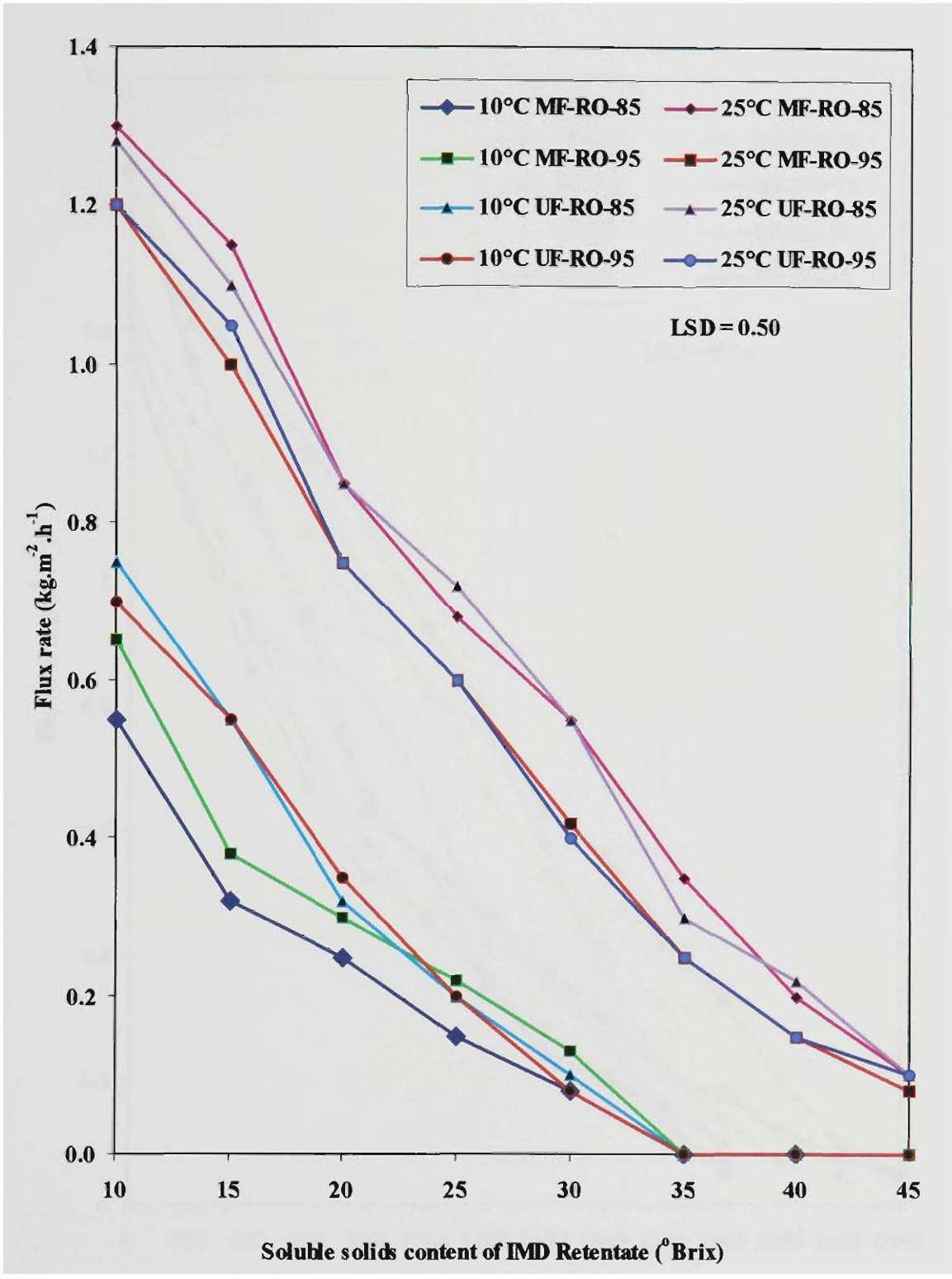


Figure 6.6 **Change in flux rate with soluble solids content during IMD concentration of clarified, preconcentrated tomato serums at 10°C and 25°C feed temperatures using Gortex XP 98007 membrane**

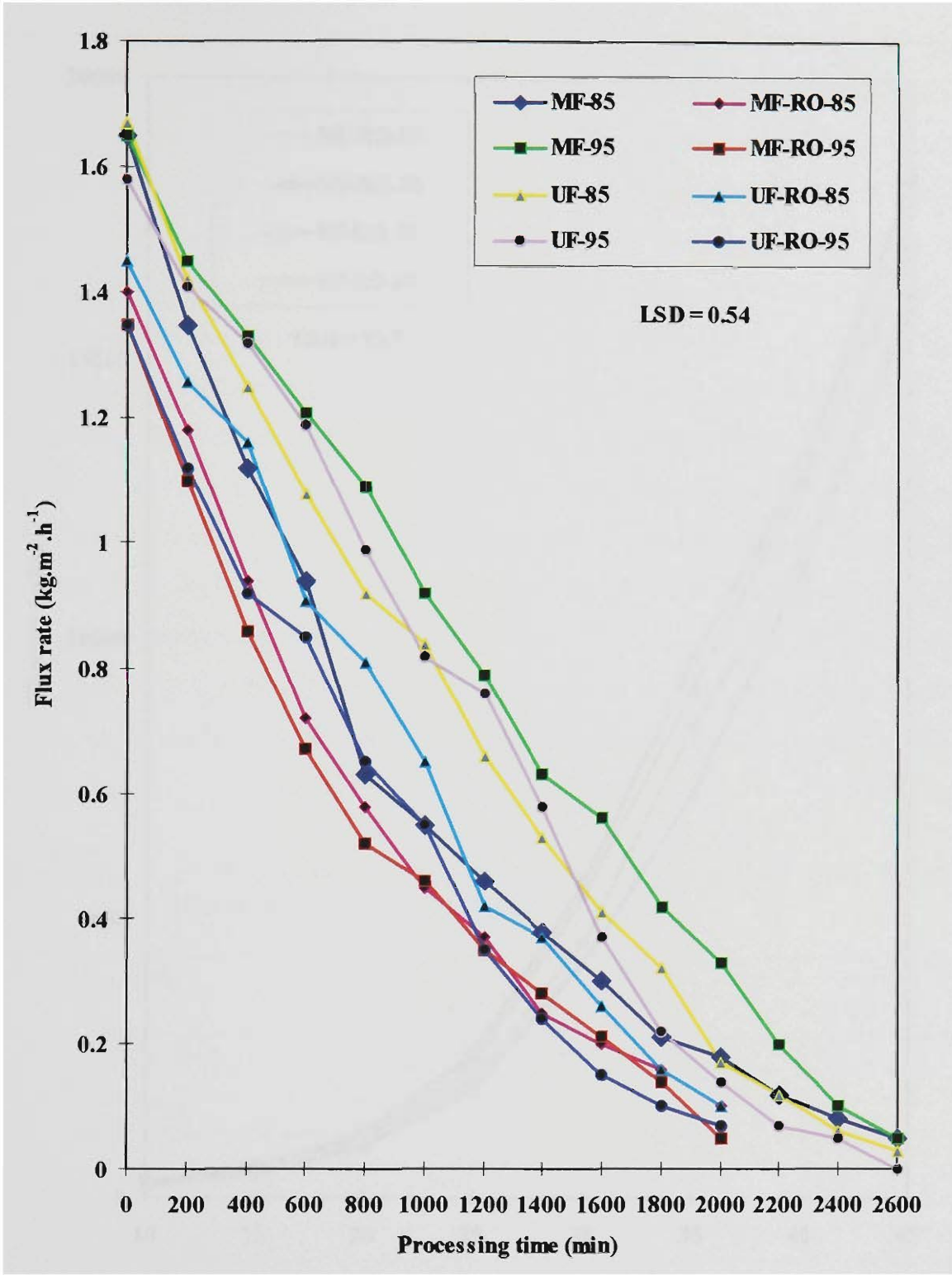


Figure 6.7 **Change in flux rate with time during IMD concentration of MF/UF clarified serums and MF/UF-RO clarified, preconcentrated serums processed at 25°C feed temperature using Gortex XP 98007 membrane**

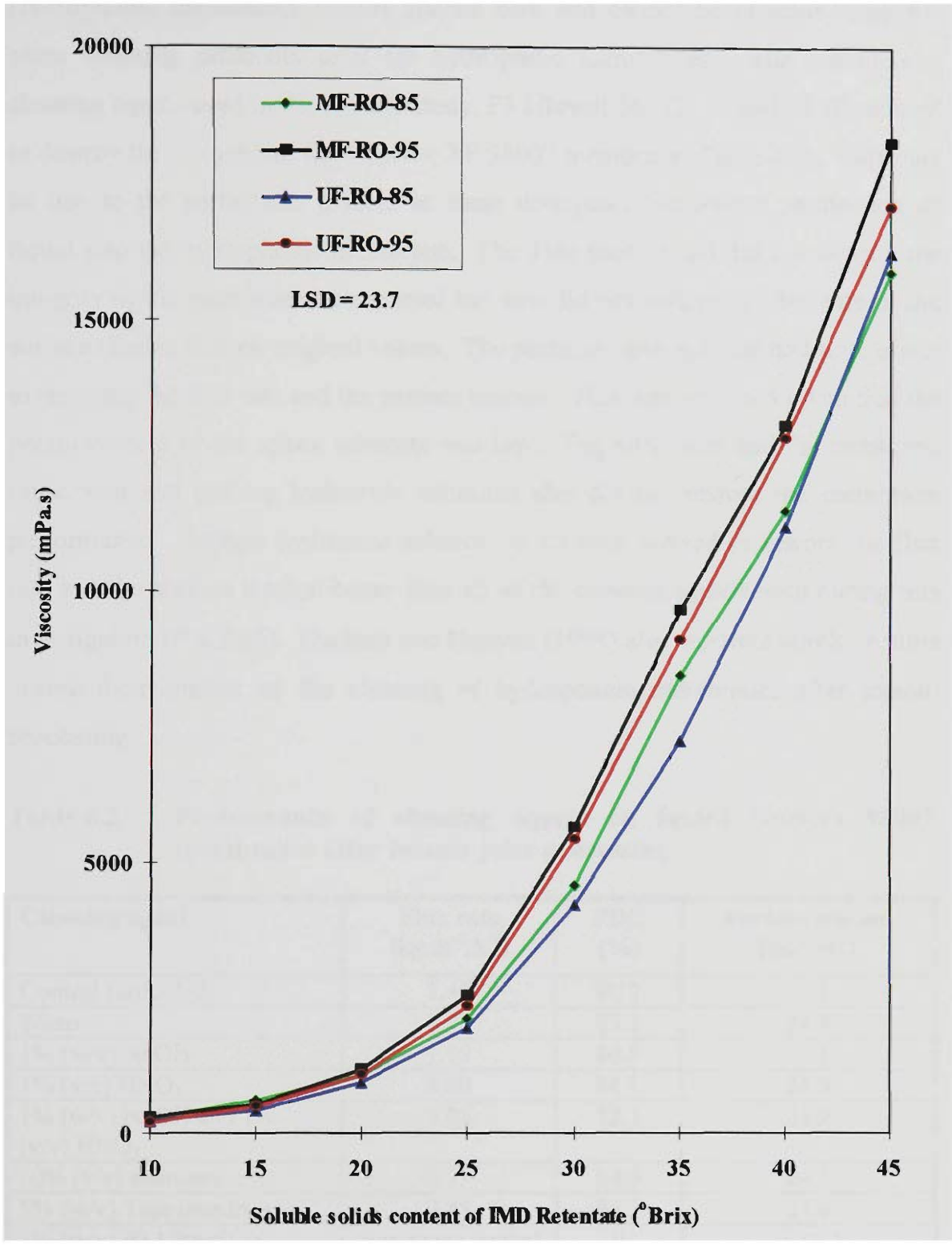


Figure 6.8 **Change in viscosity with soluble solids content of tomato serums during IMD concentration using Gortex XP 98007 membrane**

6.2.3.4. Cleaning studies

Hydrophobic membranes require special care and cannot be cleaned using the same cleaning protocols used for hydrophilic membranes. The commercial cleaning agents used in the present study, P3 Ultrasil 56, 72, 75 and 91 all seemed to destroy the integrity of the Goretex XP 98007 membrane (Table 6.2). This may be due to the surfactants present in these detergents facilitating permeation of liquid into the hydrophobic membrane. The Tide laundry aid did not destroy the integrity of the membrane as expected but also did not restore the flux rate or the surface tension to their original values. The pectinase enzyme also had little effect in restoring the flux rate and the surface tension. This was expected given that the pectin content of the serum retentate was low. The nitric acid and the combined nitric acid and sodium hydroxide solutions also did not restore the membrane performance. Sodium hydroxide solution on its own seemed to restore the flux rate and the surface tension better than all of the cleaning agents used during this investigation ($P \leq 0.05$). Durham and Nguyen (1994) also reported similar results during their studies on the cleaning of hydrophobic membranes after tomato processing.

Table 6.2 Performance of cleaning agents on fouled Goretex 98007 membranes after tomato juice processing

Cleaning agent	Flux rate ($kg.m^{-2}.h^{-1}$)	PDC (%)	Surface tension ($m.Nm^{-1}$)
Control (unfouled)	1.45	80.2	25.1
Water	0.72	85.3	24.4
1% (w/v) NaOH	1.15	80.8	25.1
1% (v/v) HNO_3	0.80	84.1	24.6
1% (w/v) NaOH and 1% (v/v) HNO_3	0.95	82.1	24.9
10% (v/v) pectinase	0.77	84.5	24.5
5% (w/v) Tide laundry aid	0.85	84.3	24.6
1% (w/v) P3 Ultrasil 56	membrane wetted	0	< 37.2
1% (v/v) P3 Ultrasil 72	membrane wetted	0	< 37.2
1% (v/v) P3 Ultrasil 75	membrane wetted	0	< 37.2
1% (v/v) P3 Ultrasil 91	membrane wetted	0	< 37.2

Standard errors: flux rate ± 0.34; PDC ± 2.88; surface tension ± 0.45

6.3. Conclusion

Tomato serums clarified by UF or MF and subsequently preconcentrated by RO required shorter IMD processing times than the corresponding UF or MF serums to achieve a given level of concentration. The serums from juices prepared at lower break temperatures had higher RO flux rates due to the lower total solids content of these serums. The UF clarified serums exhibited slightly better flux rates during RO processing than the MF clarified serums and this was due to the lower total solids content of the UF clarified serums. The spiral-wound RO plant used during this study reduced the duration of the IMD process by 10 hours as shown in Figure 6.7. The desired solids level of 45°Brix was not achieved unless the clarified serum was preconcentrated by RO. If a tubular RO system had been used, higher total solids levels than the 8.5% (w/w) level achieved in this study could have been achieved. This could have further reduced the duration of the IMD process and would be favourable in terms of delivering a better final product with respect to microbiological and chemical quality.

During IMD concentration some of the structural properties of the membranes affected the rate of water removal. Although the larger membrane pore size produced higher flux rates, the membrane material and thickness did not appear to markedly affect the flux rates. The durability of the Goretex XP 98007 made it more suitable for tomato processing than the Gelman 2TPR and Sumitomo membranes, which damaged easily during processing. The temperature variation on the feed side of the membrane significantly affected the flux rate, with higher feed temperatures producing higher flux rates. This was due to the higher kinetic energy of the water vapour molecules and reduced temperature polarisation effects at the higher feed temperature and hence faster vapour transfer rates from the feed into the brine solution. The concentration of the IMD feed also affected the flux rate considerably and the serums prepared from the unit processes (either MF or UF), when used as IMD feed, gave higher flux rates than the serums prepared by linked membrane processes (either MF-RO or UF-RO). This was due to the lower total solids content and lower viscosities of the serums prepared by unit (MF or UF) membrane processes. Although the unit membrane process serums had

higher flux rates, they required longer IMD processing times to achieve the same concentration level, and were unable to achieve the 45°Brix soluble solids level achieved with the linked membrane prepared serums. This was mainly due to the diminishing flux rate and possible fouling of the IMD membrane. The increase in soluble solids level during IMD concentration gave rise to an exponential increase in the viscosity of the serums thereby contributing to the diminishing flux rate. From this study all three variables, viz. feed temperature, feed concentration and membrane structure appear to affect the rate of water removal during IMD processing.

Hydrophobic membranes require different cleaning strategies to hydrophilic membranes. Cleaning agents containing surfactants could not be used on the hydrophobic membranes due to permeation of these agents, which 'wetted out' and destroyed the integrity of the IMD membranes. Hydrophobic membranes used for tomato juice processing can be successfully cleaned using a 1% (w/v) sodium hydroxide solution.

CHAPTER 7

Recombination and Assessment of Experimentally Prepared Tomato Pastes

7.1. Recombination studies

7.1.1. Introduction

Two new tomato pastes were prepared using membrane processes. The initial step during preparation of the new pastes involved removal of tomato solids from the serum component by centrifugation. IMD membranes can only process clarified feeds and by removing most of the tomato solids from the serum component, the membranes would be less likely to foul during the concentration processes. The solids fraction was thermally treated at 95°C and stored below -18°C so that it could be later recombined with the concentrated serum component. Either MF or UF membranes were then used to clarify the tomato serums. The MF/UF clarified serums were preconcentrated further using RO membranes and then finally concentrated using IMD membranes. The tomato solids from the centrifugation step together with those recovered from the UF/MF process were recombined with IMD concentrated serum to produce two new tomato pastes.

The objective of these studies was to prepare tomato pastes using linked membrane processes and then assess and compare these pastes with commercial pastes using physical, chemical and sensory tests. The preparation involved recombining tomato solids removed during centrifugation and clarification (Section 3.5) with clarified, concentrated serums that were obtained from the linked MF-RO-IMD and UF-RO-IMD membrane processes (Sections 3.6 and 3.7 respectively). The experimental pastes were recombined to 25% and 30% (w/w) total solids content and assessed for composition, microbiological quality, shelf stability and sensory acceptance. The lower total solids of 25% (w/w) was chosen to match the solids content of commercial pastes and the higher total solids level of 30% (w/w) paste was chosen to assess the effect of the higher level of IMD concentrate on the sensory properties of the paste.

7.1.2. Materials and methods

Two recombined tomato pastes, A1 and A2, of the UC82B variety thermally treated at 95°C and containing 25% and 30% (w/w) total solids content were prepared according to the method given in Section 3.8. The colour, consistency, ascorbic acid content, HMF content, soluble solids, titratable acidity and total solids content of the new pastes was measured according to the methods given in Sections 3.3.1.1, 3.3.1.2, 3.3.2.1, 3.3.2.2, 3.3.2.4, 3.3.2.7 and 3.3.2.8 respectively. Microbiological assessment included testing for total microbial count, yeast and mould count, Howard mould count, *Bacillus coagulans* and *Echerichia coli* and was performed according to the methods outlined in Section 3.4. The experimental pastes were also compared to commercial pastes using sensory taste panels as described in Section 3.9.

7.1.3. Results and discussion

Since there are only brief guidelines set for tomato pastes in the Australian food regulations, the quality indices used in this study to compare the recombined tomato pastes with commercial tomato pastes are similar to those routinely used by Australian commercial tomato processors. The recombined tomato pastes prepared by membrane concentration were compared with pastes prepared by thermal vacuum evaporation processes using the quality parameters summarised in Table 7.1. Although the total solids and soluble solids contents of tomato paste A1 were similar to commercial pastes, the titratable acidity and the ascorbic acid contents were considerably different. The titratable acidity level was lower and the ascorbic acid content was higher in the recombined A1 paste than in the commercial tomato pastes ($P \leq 0.05$). The higher ascorbic acid content of the recombined pastes is most likely due to the lower overall heat treatment given to these pastes. Similar titratable acidity and ascorbic acid differences were reported by Yildiz *et al.* (1993) during preparation of tomato pastes by RO and TVE processes. The lower acidity levels of membrane processed pastes was also reported by Porretta *et al.* (1992) and could be due to a number of reasons such as less oxidation of alcohols and aldehydes, deamination of amino acids and loss of soluble acids during membrane processing.

7.1.3.1. Colour

Generally colour is the most common index used for determining the final quality of tomato concentrates. The change in colour during TVE processing is usually due to browning reactions caused by the reactions between the proteins and the reducing sugars. Colour can be measured directly using a chromameter or determined by measurement of browning compounds such as furfural (F) and HMF. Although the formation of HMF does not affect the flavour (Porretta and Sandei, 1990), the reduction in the redness of the tomato paste can affect consumers' perception of the quality of the product since poor colour is often associated with poor taste. The redness value (a* value) and the red to brown ratio (a*/b*) of the tomato pastes produced by membrane concentration were higher than the values for commercial pastes produced by thermal vacuum evaporation ($P \leq 0.05$). This was expected and was due to the milder heat treatment used during membrane concentration causing less Maillard browning of the pastes. This was further confirmed by measurement of the HMF content of the pastes as shown in Table 7.1. The HMF contents of the pastes prepared by membrane processes were considerably lower than the HMF contents of the pastes produced by thermal vacuum evaporation processes even though the pastes produced by membrane concentration had to be heated after recombination to ensure microbiological quality requirements.

7.1.3.2. Consistency

The measurement of texture is a routine test used by tomato processors to describe the consistency of tomato concentrates. Generally tomato concentrate texture can be determined using either viscometers or consistometers. While the viscometers measure the intrinsic texture of the tomato paste, which is related to the inactivation of pectic enzymes during the break processes, the consistometer measures the extrinsic texture which is related to the flow properties of the paste. The viscosity and the consistency are related, however the factors that often affect viscosity may not necessarily affect the consistency of the tomato paste. Although the high total solids and pectic substances improve the consistency, other external

factors such as homogenization of the tomato juice prior to concentration can also improve consistency.

Table 7.1 Quality characteristics measured in recombined (A1 and A2) and commercial tomato pastes

Quality indices	Paste A1	Paste A2	Commercial B	Commercial C
Soluble solids (°Brix)	22.8	26.9	23.5	22.8
Total solids (% w/w)	25.1	30.0	26.7	25.5
Titratable acidity (g/100g) citric acid	1.25	1.36	1.47	1.38
Ascorbic acid (mg/100mL)	53	58	33	26
Bostwick consistency (flow cm in 30s at 20°C)	10.4	8.2	7.0	7.9
Colour L*	29.03	29.70	30.14	28.71
a*	+30.38	+30.22	+28.30	+24.28
b*	+20.39	+21.28	+21.04	+19.18
a*/b*	1.49	1.42	1.34	1.26
Hydroxymethylfurfural (ppm)	19.4	23.1	32.5	36.7

Standard errors: soluble solids ± 0.66; total solids ± 0.46; titratable acidity ± 0.06; ascorbic acid ± 6.60; Bostwick consistency ± 0.85; colour a*/b* ± 0.22; hydroxymethylfurfural ± 1.24

The consistency of the recombined pastes and commercial pastes was measured using a Bostwick consistometer (Section 3.3.1.2). As shown in Table 7.1, the Bostwick consistency value of tomato paste A1 was approximately 50% greater than that of commercial paste B and approximately 30% higher than that of commercial paste C, suggesting paste A1 had poorer texture (thinner) than the commercial samples ($P \leq 0.05$). The consistency value of tomato paste A2 however, was only slightly higher than that of the commercial pastes and this would suggest that the texture of paste A2 was not very different to the commercial pastes B and C. The improved texture of A2 was most likely due to its higher solids content arising from the higher level of IMD concentrate used in its preparation. During sensory comparison of texture, there were no differences noted between the texture of pastes A1 and A2. This suggests that the differences

in texture may not be a limiting sensory parameter at all. The difference in the consistencies of the membrane processed pastes compared to thermally concentrated pastes was also noted by Poretta *et al.* (1992) and Yildiz *et al.* (1993) and could be due to pectin-protein interactions and the loss of pectins due to fouling during membrane processing. The consistency results obtained during the present study confirm the results obtained by Porretta *et al.* (1992) and Yildiz *et al.* (1993).

7.2. Microbiological assessment of recombined pastes

7.2.1. Introduction

Preparation of tomato pastes by membrane processes can produce products of superior organoleptic properties to those produced by thermal concentration processes. However, the microbiological status and stability of these products is particularly important since they are processed at lower temperatures for long periods thereby providing greater potential for microbial outgrowth. An advantage of using MF and UF membrane processes for juice clarification, such as was done during this study (Section 3.5.2), is that they can potentially reduce the total microbial load of the final product since they can filter out microorganisms from the permeate. During this study all the fractions except the RO permeate were used for the subsequent recombination step, hence the opportunity for removing microorganisms was minimal.

During the manufacture of tomato paste, the microbial load of the final product is dependent on the initial load in the tomato juice and the hygienic practices used during processing. Ideally the microbiological assessment of tomato pastes should be based on current Australian standards, where available, or on suitable industry standards. The Australian microbiological standards listed for tomato pastes only prescribes a Howard mould count, therefore most of the microbiological tests performed in this study were guided by the general microbiological procedures listed in the Australian Standards and by the internal industry standards obtained from a leading tomato paste manufacturer. The tomato pastes manufactured commercially are only routinely tested for total

microbial counts and Howard mould counts. During this study however, additional microbiological tests were carried out to investigate how low temperature membrane processing affected the microbiological status of the final paste.

This study investigated the microbiological status of tomato pastes prepared by traditional thermal vacuum evaporation processes and by the new membrane concentration processes. In order to compare the results obtained from the two processes, all the intermediate products obtained during processing were tested for selected microorganisms and for yeasts and moulds.

7.2.2. Materials and methods

Usually total microbial and Howard mould counts are the only microbiological tests done on commercial tomato pastes. During this study, additional tests for yeasts and moulds, *Bacillus coagulans* and *Escherichia coli* were carried out to investigate whether low temperature membrane processing affected final product microbial loads. *Bacillus coagulans* was tested because it is a common organism found in soil and has been previously isolated from canned tomatoes and tomato juice (Segmiller and Evancho, 1992). *Escherichia coli* was tested because it is often associated with post-processing contamination. The total microbial, yeast and mould, Howard mould, *Bacillus coagulans*, *Coliforms* and *Escherichia coli* counts were carried out in duplicate and according to the methods described in Sections 3.4.1, 3.4.2, 3.4.3, 3.4.4 and 3.4.5 respectively.

7.2.3. Results and discussion

The microbiological results for the intermediate products obtained during linked membrane processing of tomato juice and for final recombined pastes and commercial pastes are summarised in Table 7.2. The tomato juice obtained after the hot break process still contained yeasts and moulds as indicated by both the yeast and mould count and Howard mould count. During the centrifugation of the tomato juice into tomato solids and serum, there appears to be a preferential concentration of microorganisms in the solid fraction as indicated by total, yeast and mould, and Howard mould counts. After centrifugation the serum fraction

was processed by either microfiltration or ultrafiltration and the resulting permeate showed absence of microorganisms. This was seen as an advantage since the permeate fractions were to be used for subsequent RO and IMD processing. The absence of microorganisms in the MF and UF permeates was due to the small pore size of the membrane restricting the passage of bacteria, yeasts and moulds. The sanitation (with acidified sodium metabisulphite) and enclosure of the MF/UF system during processing also may have contributed to the absence of microorganisms. The reoccurrence of microorganisms during reverse osmosis was most likely due to the difficulty in enclosing the RO system during processing as well as the withdrawal of sanitation procedures prior to RO processing since the RO membranes appeared to be sensitive to the acidified sodium metabisulphite.

The increased microbial count of the IMD concentrate was due to concentration of the microbial load of the RO feed by the IMD process and not due to the accelerated growth of microorganisms *per se*. Since the IMD process operates at ambient temperature, higher microbial counts might have been expected in the IMD concentrate but this was not observed. The additional procedures of sanitizing and enclosing the system may have prevented the further growth of organisms. The absence of moulds as determined by the Howard mould count, in the RO concentrate but its appearance in the IMD concentrate was an interesting and unexpected result since additional safety and sanitation procedures were followed during IMD processing. However, this was most likely due to the concentration of the tomato serum since the bacterial count increased by the same factor as the concentration factor. Although the recombined tomato pastes prepared by IMD concentration had lower Howard mould counts than the commercial pastes, they had higher yeast and mould counts ($P \leq 0.05$) and this could have been due to the lower temperatures used during linked membrane processing failing to destroy all yeasts and moulds. By using linked membrane processes the total microbial load of the final product was reduced to 50% and the Howard mould count to 25% of that found in commercial tomato pastes ($P \leq 0.05$). The safety measures of sanitation and enclosure of the product during

membrane processing probably helped in reducing the overall growth of microorganisms. The lower microbial count of the experimental pastes requires further investigation and should be confirmed by processing trials on a commercial scale.

During commercial tomato paste preparation the Howard mould count is the indicator for product quality, however this study was based on low temperature membrane processing therefore additional indicators such as *Escherichia coli* and *Bacillus coagulans* were used to investigate microbiological quality. Both of these organisms were absent which indicated that low temperature membrane processing did not jeopardize the microbiological quality and safety of the product

Table 7.2 Microbiological assessment of final and intermediate products produced during the preparation of tomato pastes by linked membrane (Pastes A1 and A2) and thermal vacuum evaporation processes (Pastes B and C)

Product	Total microbial count (cfu/g or cfu/mL)	Yeast and mould count (cfu/g or cfu/mL)	Howard Mould count (%)	*Bacillus coagulans* cfu/g	*Escherichia coli* MPN/g
Tomato juice	20	2	20	-	-
Tomato solids	15	2	12	-	-
Tomato serum	10	-	10	-	-
MF permeate	-	-	-	-	-
UF permeate	-	-	-	-	-
RO concentrate	2	2	0	-	-
IMD concentrate	15	10	5	-	-
Recombined Paste A1	15	10	5	0	0
Recombined Paste A2	14	10	5	0	0
Commercial Paste B	25	5	20	0	0
Commercial paste C	32	2	30	0	0

Standard errors: total microbial count ± 3; yeast and moulds ± 2; Howard mould count ± 1;

7.3. Sensory assessment of recombined pastes

7.3.1. Introduction

Sensory assessment is widely used in market research to determine the acceptability of new products or of variations to existing products. Since high costs are associated with developing and launching a new product, taste panels are an informative way of investigating the likelihood of success of the new product before it is introduced on the market. Sensory evaluation involves the assessment of product features such as colour, aroma, texture and flavour. The tomato pastes manufactured during this study had similar composition to existing brands but were prepared using different processing strategies.

The purpose of this investigation was to assess the acceptability of the new tomato pastes using the common sensory properties of colour, aroma, texture and flavour. The acceptability of the new pastes was compared to commercial pastes using hedonic rating scales. Statistical comparison between the pastes was made using the analysis of variance test.

7.3.2. Materials and methods

The two experimental recombined tomato pastes A1 and A2 (prepared by the strategies given in Section 3.8 from the UC82B variety at 95°C break temperature) and the two commercial pastes B and C were assessed for colour, aroma, texture and flavour according to the methods described in Section 3.9.1. The experimental and commercial pastes were also assessed for colour and taste only on a pizza base as described in Section 3.9.2. All the results were statistically analysed as described in Section 3.9.3.

7.3.3. Results and discussion

The results of the statistical analysis of the taste panel results from the comparison of the recombined pastes A1 and A2 with commercial pastes B and C are summarised in Tables 7.3, 7.4 and 7.5. The colour of the recombined pastes A1 and A2 and commercial pastes B and C and of pizzas prepared with A1, A2, B and C tomato pastes is also presented photographically in Figures 7.1 and 7.2 respectively.

The recombined pastes A1 and A2, whether sampled as pastes or on a pizza base, had a brighter red colour (Figures 7.1 and 7.2) and were preferred over the duller red colour of commercial pastes B and C. The colour preferences noted during the panel sessions is supported by the data reported in Table 7.1 which showed pastes A1 and A2 as having higher a* values and a*/b* ratios (redness values) and lower HMF contents than commercial pastes B and C. Statistically the colour of the recombined tomato pastes A1 and A2 was significantly different from ($P \leq 0.05$) and preferred over the colour of commercial pastes B and C. There were no significant differences ($P > 0.05$) noted for colour when pastes A1 and A2 were compared or when commercial pastes B and C were compared. The colour of the pizzas made from tomato pastes A1 and A2 was significantly different from ($P \leq 0.05$) and preferred to pizzas made with commercial pastes B and C. Similarly there were no significant differences ($P > 0.05$) in the colour of pizzas when pastes A1 and A2 were compared and pastes B and C were compared. The better colour of pastes A1 and A2 was due to the lower temperatures used during the processing and manufacture of these pastes. The lower processing temperatures resulted in reduced pigment discolouration and browning compound formation as reflected in the lower HMF levels in these pastes compared to the commercial pastes (see Table 7.1).

The aroma of paste A1 was also noted as superior to and preferred over the aromas of commercial pastes B and C while that of paste A2 was also superior to and preferred over commercial paste C ($P \leq 0.05$). There was no significant difference noted between the aromas of paste A1 and A2 or between pastes B and C ($P > 0.05$). The overall superiority in aroma of pastes A1 and A2 is most probably due to the reduced loss of volatile components associated with the lower heat processes used during the manufacture of these pastes, hence giving them an advantage over current commercial pastes.

Table 7.3 Summary of the statistical analysis of the sensory comparison of recombined tomato paste A1 with commercial tomato pastes B and C

Sensory parameter	A1* vs B		A1* vs C		B* vs C	
	Difference of means	Calculated F value	Difference of means	Calculated F value	Difference of means	Calculated F value
Colour of paste	1.80[a]	8.55	1.32[a]	10.34	0.48[b]	1.25
Aroma of paste	1.28[a]	5.40	1.24[a]	4.50	0.04[b]	2.26
Texture of paste	0.80[b]	1.66	1.12[a]	5.35	0.32[b]	1.85
Flavour of paste	0.08[b]	2.24	2.16[a]	7.55	1.08[b]	0.65
Colour of pizza	1.80[a]	9.24	1.32[a]	11.25	0.48[b]	0.35
Taste of pizza	1.08[b]	2.50	2.04[a]	8.90	0.96[b]	2.85

ANOVA Test (one-way), statistical significance level $P \leq 0.05$; n = 25, Table F value = 3.15; Difference of means was performed using Tukey's test.
*Panel preferred sample; a = significant ($P \leq 0.05$); b = not significant ($P > 0.05$)

Table 7.4 Summary of the statistical analysis of the sensory comparison of recombined tomato paste A2 with commercial tomato pastes B and C

Sensory parameter	A2* vs B		A2* vs C		B* vs C	
	Difference of means	Calculated F value	Difference of means	Calculated F value	Difference of means	Calculated F value
Colour of paste	2.32[a]	7.26	2.04[a]	6.55	0.28[b]	1.56
Aroma of paste	0.60[b]	1.76	1.04[a]	11.47	0.44[b]	2.25
Texture of paste	1.40[a]	6.66	0.80[b]	1.45	0.60[b]	1.95
Flavour of paste	1.96[a]	9.24	2.36[a]	6.52	0.82[b]	2.24
Colour of pizza	1.68[a]	5.55	2.04[a]	10.24	0.36[b]	0.75
Taste of pizza	1.04[b]	2.16	2.12[a]	5.78	1.06[b]	2.14

ANOVA Test (one-way), statistical significance level $P \leq 0.05$; n = 25, Table F value = 3.15; Difference of means was performed using Tukey's test.
*Panel preferred sample; a = significant ($P \leq 0.05$); b = not significant ($P > 0.05$)

Table 7.5 Summary of the statistical analysis of the sensory comparison of recombined tomato pastes A1 and A2

Sensory parameter	Calculated F value
Colour of paste	0.15
Aroma of paste	2.43
Texture of paste	0.33
Flavour of paste	0.13
Colour of pizza	0.90
Taste of pizza	0.05

ANOVA Test (one-way), statistical significance level $P \leq 0.05$; $n = 25$, Table F value = 4.28

The texture of the tomato pastes usually can be correlated with and discussed in terms of consistency. The consistency value of paste A1 reported in Table 7.1 was 27%, 48% and 32% higher than pastes A2, B and C respectively ($P \leq 0.05$). However the panel did not detect any consistency difference between pastes A1 and A2 when they were individually sampled or between pastes A1 and B ($P > 0.05$). Yet paste C, while assessed by the panels as not being significantly different to paste B and having a very similar Bostwick value to paste A2, was seen as being significantly different to paste A1. Also, although paste A2 had a similar consistency value to those of the commercial pastes and paste C in particular, the panel still noted differences in texture between pastes A2 and B ($P \leq 0.05$). These inconsistencies in correlation of consumer perception of texture, as assessed by the taste panels, with instrumental assessment of texture (as assessed by consistency measurement) would suggest that instrumental methods of assessment are of only limited value in predicting consumers' perceptions of paste textural qualities. However, to verify this a much more detailed study of sensory and instrumental assessment of tomato paste texture, including alternative instrumental assessment methods, would need to be undertaken. Such a study was considered outside the brief of this present study.

The flavour of paste A1 was significantly different from ($P \leq 0.05$) and preferred more than the flavour of paste C, but had equal preference to paste B. Also, at the same significance level, no flavour preference was noted between pastes B and C. The flavour of paste A2 was assessed as being significantly better ($P \leq 0.05$) than pastes B and C. The flavours of pastes A1 and A2 were assessed by the panelists as not being significantly different.

The colour of the pizzas made with pastes A1 and A2 were significantly different to ($P \leq 0.05$) and preferred over the colour of the pizzas made with pastes B and C. The taste of the pizzas made with pastes A1 and A2 were not significantly different ($P > 0.05$) to the pizzas made with paste B, but were significantly different and preferred to the taste of pizza made with paste C (at the same significance level). The colour and taste comparison between pizzas made with pastes A1 and A2 showed no significant differences ($P > 0.05$). Similarly the colour and taste of pizzas made with pastes B and C were equally preferred.

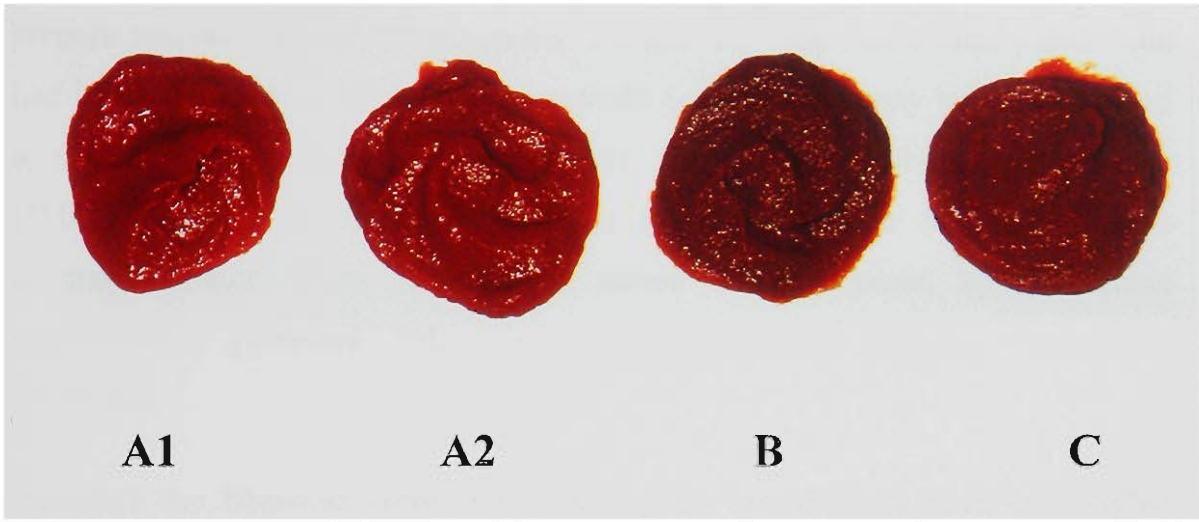


Figure 7.1 **Photographic comparison of recombined pastes A1 and A2 and commercial pastes B and C**

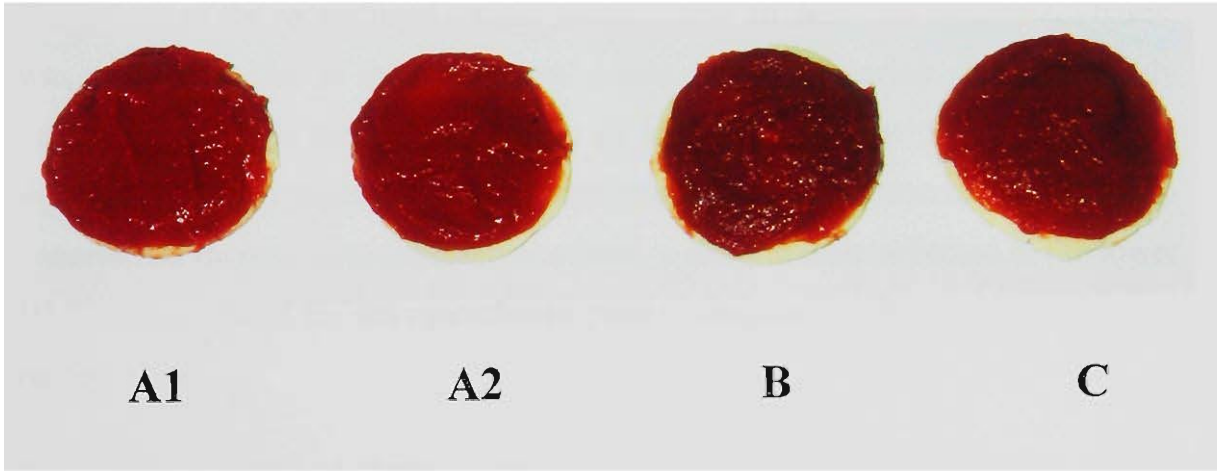


Figure 7.2 **Photographic comparison of pizzas made with recombined pastes A1 and A2 and commercial pastes B and C**

7.4. Conclusion

Recombination of tomato solids with IMD concentrated serum was used to prepare two recombined tomato pastes, A1 and A2. The recombined pastes both had lower titratable acidity than commercial pastes, which may have contributed to their overall preference by the panelists. The higher ascorbic acid and lower HMF contents of the recombined pastes supports the view that there is less thermal damage when the tomato pastes were prepared by membrane concentration processes rather than by the traditional vacuum evaporation processes.

Although the Bostwick consistency value of the recombined pastes was higher than that of commercial pastes, suggesting poorer texture or consistency, these differences in texture were not detected by panelists during the sensory assessment of the pastes. This apparent lack of correlation between panel and instrumental assessment of texture potentially raises questions about the usefulness of the Bostwick Consistometer to assess the textural quality of paste.

The colour of the recombined tomato pastes, either on their own or on pizza bases, was superior to that of the commercial pastes. As noted earlier, this is probably due to the reduced thermal production of browning compounds, such as HMF, during the low temperature membrane concentration processes compared to commercial thermal evaporation procedures; a result further reflected in the lower HMF values found for the recombined pastes compared to the commercial brand pastes.

When the recombined tomato pastes were assessed for microbiological quality, they were found to have superior overall microbiological quality to the commercial pastes. This was most likely due to the secondary clarification step, using either MF or UF, reducing the microbial load of the permeate, and the subsequent use of this permeate fraction for further processing by RO and IMD processes. Also, only a small quantity of MF or UF concentrate was used during the recombination process, which also may have contributed to the lower microbial counts.

Overall both pastes A1 and A2 had better colour than commercial pastes B and C. The flavour of paste A2 was better than both of the commercial pastes B and C, however the flavour of A1 was only better than paste C. Although paste A1 had better colour and aroma than paste B, it had very similar flavour and texture to paste B. Statistically there were no differences noted in colour, aroma, texture and flavour between pastes A1 and A2.

CHAPTER 8

General Conclusions

8.1. Summary of results

Tomatoes are generally consumed as fresh produce or processed into concentrates for use out of season. The composition of tomatoes is important for processing and is affected by variety, climatic conditions, seasonal variation and disease. In Australia, approximately 85% of the tomato crop is processed into juice, sauce and paste by means of thermal vacuum evaporation (TVE) processes with the remainder going to the fresh trade. The high temperatures used for water removal by evaporation can often damage heat sensitive aroma and flavour components as well as cause discolouration of the final concentrates. While volatile components are lost, additional browning compounds such as furfural (F) and hydroxymethylfurfural (HMF) are also formed during these TVE processes. Although HMF and F do not affect the flavour of processed tomato products, they do adversely affect the colour. Due to the increasing demand for tomato concentrates of better sensory qualities, alternative concentration methods have been the subject of investigation.

This study investigated the use of low temperature linked membrane processes, with particular emphasis on isothermal membrane distillation (IMD), for the concentration of tomato juice to paste as an alternative to the TVE processes commonly used at present. Currently the use of IMD in food concentration is limited to clarified food products and this project sought to develop and investigate an appropriate strategy to enable its use with particulate containing foods such as tomato juice. A processing strategy based on fractionation of the tomato juice into serum and solids components followed by concentration of the serum by IMD and subsequent recombination of the concentrated serum with the original juice solids was adopted.

This study comprised four distinct stages:

1. **Thermal inactivation studies on the deteriorative enzymes in tomatoes**

   This stage involved an investigation of the thermal stability characteristics of the three main deteriorative enzymes involved in tomato processing, viz. Peroxidase (PO), Pectinmethylesterase (PME) and Polygalacturonase (PG), in order to establish the minimal thermal break schedule necessary to effectively inactivate these enzymes.

2. **Studies on the fractionation and clarification of tomato juice**

   Since currently IMD can only effectively handle clarified feeds, this stage sought to identify and evaluate appropriate techniques to fractionate and clarify tomato juice. A process involving primary fractionation or clarification by centrifugation followed by secondary clarification using MF and UF processes was adopted.

3. **Studies on the preconcentration and concentration of tomato juice serum**

   This stage investigated the use of RO to preconcentrate clarified tomato juice serum and the subsequent concentration of this preconcentrated serum by IMD at 10°C and 25°C.

4. **Recombination and product evaluation studies.**

   Stage 4 involved the physical, chemical, microbiological and sensory evaluation of tomato pastes prepared by recombination of tomato solids from primary and secondary clarification operations with IMD concentrated serums. The experimental pastes were evaluated against two leading commercial tomato pastes.

8.1.1. Thermal inactivation of deteriorative enzymes

The traditional 'break process' used commercially for deteriorative enzyme inactivation in tomato processing involves the use of high temperatures in excess of 95°C and for periods of up to thirty minutes. Although the break process is necessary for enzyme inactivation, the high temperatures used and the duration of

the process are often unnecessary since they are in excess of what is required to achieve inactivation. During this investigation the three deteriorative enzymes of particular concern were studied in two processing varieties of Roma tomatoes, viz. UC82B and Alta. The two varieties differed in composition as well as in PO, PME and PG enzyme contents. During the same growing season the UC82B variety had higher titratable acidity and total solids than the Alta variety. Also, seasonal variation studied in the UC82B variety showed that during the low rainfall season tomatoes had higher total solids levels than tomatoes from the higher rainfall season. Due to unavailability of the Alta variety in the second growing season, seasonal variation could not be studied for the Alta variety.

The UC82B and Alta tomatoes were thermally treated at two different break temperatures of 85°C and 95°C. However, due to the limited availability of the Alta variety, only the UC82B variety was used for subsequent clarification and membrane processing trials. In the UC82B variety, the juice obtained from the 85°C break temperature had lower viscosity, suspended solids, soluble solids and total solids than that obtained from the 95°C break process.

The heat stability of the enzymes or the F/D values from the two varieties studied is summarised in Table 4.4. The PME enzyme from the UC82B variety was found to be the most heat stable enzyme having the highest F/D value of 2.80, followed by the PG enzyme from both the varieties with a F/D value of 2.75. The PME enzyme from the Alta variety, having a F/D value of 2.65, was easier to inactivate than the PME enzyme from the UC82B variety. The PO enzyme from both of the varieties had low F/D values and therefore it appears that inactivation of this enzyme may not be of major importance in tomato processing.

Based on this study, it is proposed that the thermal break process parameters should be based on inactivation of PME, since it is the most heat stable enzyme, rather than on some of the other enzymes, e.g. PO, present in tomatoes. The recommended minimum D process required to achieve PME inactivation for both of the varieties is 3.5 minutes at 87.5°C. However this recommendation should be confirmed by commercial scale trials.

8.1.2. Primary and secondary clarification of tomato juice

Traditional TVE processes concentrate tomato juice without separation into solids and serum components. However IMD can only process clarified feeds hence different processing strategies had to be used and the tomato juice was initially clarified. Clarification of the juice was achieved in two stages. The first involved primary clarification by centrifugation, which yielded tomato solids and tomato serum components. The second stage involved secondary clarification of the tomato serum by MF or UF membrane processes. This secondary clarification step was necessary because the serum obtained from centrifugation still contained suspended solids and therefore could not be effectively processed by RO, or by IMD in particular.

The MF and UF processes both proved to be effective for secondary clarification, removing more than 80% of the suspended solids from the tomato serum. At the same membrane processing temperatures, the MF process gave higher flux rates and was less prone to fouling than the UF process and therefore was initially considered more suitable for tomato juice clarification. However, during subsequent RO and IMD membrane processing operations it was found that the UF clarified serum gave better flux rates than the MF clarified serum. Consequently, overall the UF process may be more suitable for the linked membrane processing of tomato serum than the MF process.

8.1.3. Preconcentration and concentration of tomato serum

The MF and UF permeates obtained during secondary clarification were either directly concentrated by the IMD process, or initially preconcentrated by RO and then subsequently concentrated by IMD. When the MF and UF permeates were directly concentrated by IMD, the IMD flux rates were higher due to the initial lower total solids content of these feeds. Although the flux rates of the MF-IMD and UF-IMD feeds were initially higher than the linked MF-RO-IMD and UF-RO-IMD feeds, the IMD processing times were longer to achieve comparable concentration levels. This was a major drawback of unit processing. Also the unit processing did not achieve the desired soluble solids level of 45°Brix, which could

only be achieved by two stage processing using linked RO-IMD processes.

In addition to IMD feed concentration other processing parameters, such as membrane material and processing temperatures, also affected the performance of the IMD process. During the study of five different types of membranes, it was found that the pore size significantly affected the IMD flux rates while the membrane material and membrane thickness only marginally affected the flux rates. The Goretex membrane 98007 was determined to be the most suitable for tomato processing due to its resilience and high flux rates during processing. Other membranes that had high initial flux rates appeared to lack durability. Their poor performance was due to structural problems such as absence or separation of backing material. The investigation of processing temperatures (feed side) indicated that, as expected, higher temperatures (25°C) gave better flux rates and therefore were preferred for IMD processing. The use of higher processing temperatures did not appear to adversely affect the overall microbiological quality of the product.

Cleaning studies were performed on the Goretex 98007 membrane using various cleaning agents containing alkali, acid, surfactants, phosphates and enzymes, either alone or in combination. Most of these cleaning agents did not restore the flux rate to its original value. The detergent and surfactant based cleaners 'wetted' out and damaged the membrane. The most effective cleaning agent for the Goretex 98007 membrane was found to be a 1% (w/w) sodium hydroxide solution.

8.1.4. Recombination and product evaluation

Two tomato pastes, A1 and A2, with total solids levels of 25% (w/w) and 30% (w/w) respectively, were prepared by recombination of IMD serum concentrates and the tomato solids obtained from juice clarification by centrifugation and MF/UF membrane processes. These and two commercial pastes were assessed by physiochemical and sensory tests. The recombined pastes both had lower titratable acidity than the commercial pastes and this may have been due to loss of water-soluble acids during membrane concentration. The higher ascorbic acid and

lower HMF contents indicated that the recombined pastes suffered less thermal damage during processing than the commercial tomato pastes, which had been prepared by TVE processes. The recombined pastes also had better colour (higher a*/b* values) than the commercial pastes and this was also due to the milder heat treatment used during preparation of these pastes.

The recombined pastes were also compared to commercial pastes by means of taste panels and the sensory properties of colour, aroma, texture and flavour were assessed. Although the recombined paste A1 had better colour and aroma than the two commercial pastes B and C, the texture and flavour were not significantly different to paste B but were significantly different and preferred to paste C (at $p \leq 0.05$ level). Paste A2 had better colour, aroma and flavour than both of the commercial pastes sampled, however the texture of paste A2 was significantly different and preferred to B but not to paste C (at $p \leq 0.05$ level). The recombined pastes had poorer textures than the commercial pastes as determined by their higher Bostwick values, however this difference could only be detected by some of the sensory panelists. In terms of colour, the pizzas made from the recombined pastes were preferred to the pizzas made from the commercial pastes.

The microbiological assessment of recombined and commercial pastes showed that recombined pastes had a 50% lower total microbial count and up to 75% lower Howard mould count than the commercial pastes. The lower microbial counts were largely due to the use of MF or UF processes during the secondary clarification stage. The yeast and mould count however, was higher in the recombined paste than the commercial paste and was due mainly to the extended hours of IMD processing at ambient temperature. In order to reduce the duration of the IMD process, the IMD feed should be preconcentrated to the highest possible solids level. Overall however, the microbiological quality of the recombined products was superior to that of the commercial products.

8.2 Future studies

The objectives of this study were achieved and improved tomato pastes were prepared using the proposed linked membrane processes. Tomato pastes prepared by the new processing strategy using membrane technology had better colour, flavour and aroma than current leading commercial brands of tomato paste. Although this was a good result certain factors may limit the development of this new processing strategy on an industrial scale. The capital costs involved with installation of various membrane types may outweigh the benefits of producing tomato pastes of improved sensory properties. Other drawbacks include the duration of the IMD process itself and the unavailability of IMD membranes locally.

This study investigated thermal break processes for inactivation of deteriorative enzymes. Other methods of enzyme inactivation such as microwave processes and pressure-induced processes should also be investigated.

During this study tomato juice was fractionated into solids and serum components to allow concentration by IMD process. The fractionation of juice was achieved by centrifugation, followed by secondary clarification by MF or UF processes. The MF and UF membranes used for this investigation were of a hollow fibre design. Further studies should be conducted using a tubular design that would be more suitable for particulate containing juices such as tomato. Similarly the RO membranes used for preconcentration of tomato permeates were of a spiral-wound design and as a result only concentrated the juice serum to 8.5% (w/w) total solids level. Further studies should be conducted using tubular RO membranes that have the ability of concentrating to higher concentration levels hence reducing the duration of the IMD process.

IMD concentration at present is restricted to clarified juice feeds due to the limitations of the membrane materials. During this investigation only five membrane types were used for IMD concentration. Further work needs to be done using alternative membrane materials. Also some of the membranes examined in this study had major structural problems and the manufacturers of these

membranes should be contacted so that improvements can be made in the design of these membranes. The work done in this study involved the use of a plate and frame designed IMD plant and the use of alternative designs such as a tubular design should be investigated and may allow concentration to higher total solids levels than was achieved in this study.

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Appendix 1

Typical tomato paste sensory evaluation sheet

Colour of Paste	**A**	**B**	**C**
Like extremely			
Like very much			
Like moderately			
Like slightly			
Neither like nor dislike			
Dislike slightly			
Dislike moderately			
Dislike very much			
Dislike extremely			
Aroma of paste			
Like extremely			
Like very much			
Like moderately			
Like slightly			
Neither like nor dislike			
Dislike slightly			
Dislike moderately			
Dislike very much			
Texture of paste			
Extremely good			
Very good			
Good			
Just above average			
Satisfactory			
Just below average			
Poor			
Very poor			
Extremely poor			
Flavour of paste			
Like extremely			
Like very much			
Like moderately			
Like slightly			
Neither like nor dislike			
Dislike slightly			
Dislike moderately			
Dislike very much			
Dislike extremely			

Appendix 2

Typical pizza sensory evaluation sheet

Colour of pizza	**A**	**B**	**C**
Like extremely			
Like very much			
Like moderately			
Like slightly			
Neither like nor dislike			
Dislike slightly			
Dislike moderately			
Dislike very much			
Dislike extremely			
Taste of pizza			
Like extremely			
Like very much			
Like moderately			
Like slightly			
Neither like nor dislike			
Dislike slightly			
Dislike moderately			
Dislike very much			
Dislike extremely